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of the
Society of Dyers and Colourists

Volume 73 Number 11

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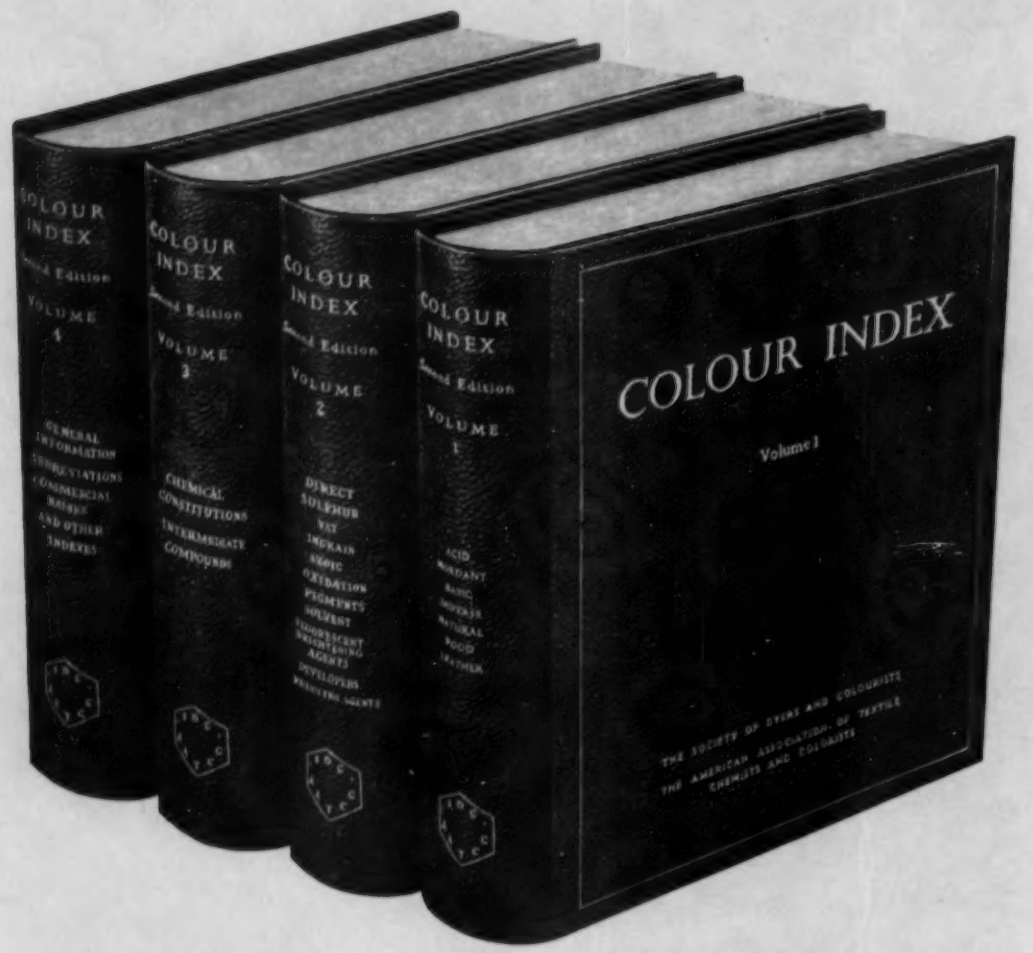

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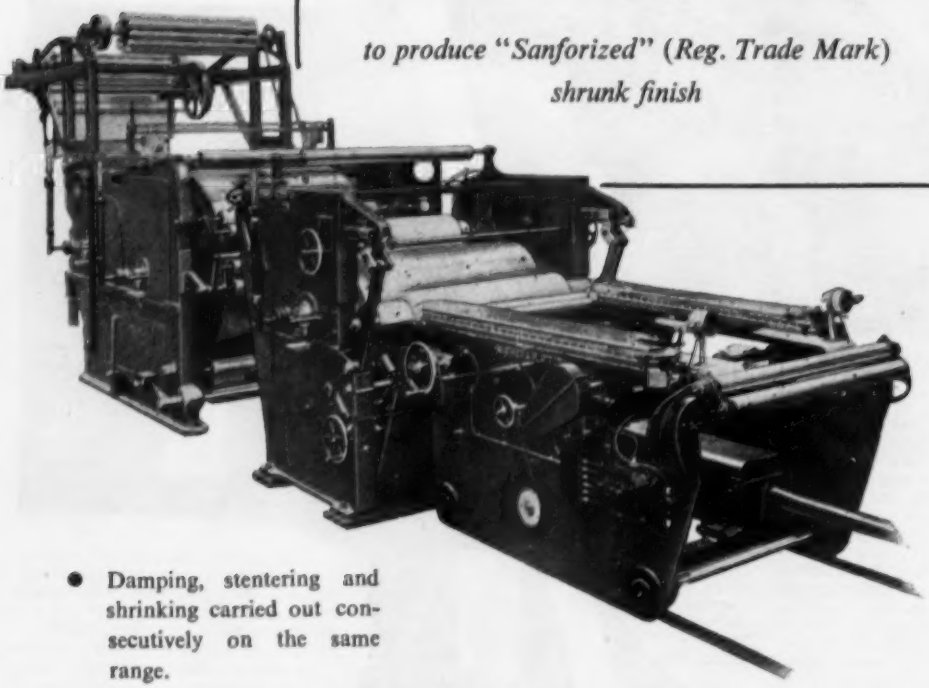

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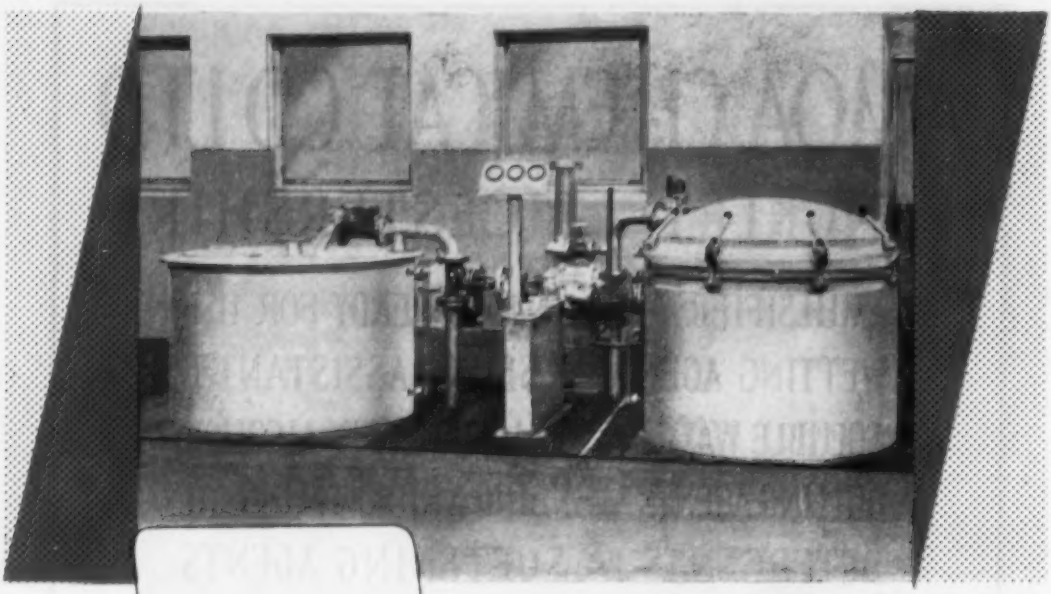

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–7 of the January 1957 and pages 285–290 of the July 1957 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Application of Colour Physics to Textiles — *J. C. Guthrie and P. H. Oliver*

The Application of Pigments to Textiles — *W. Kass*

Levelling Problems in Vat Dyeing — *H. Musshoff*

COMMUNICATIONS

Studies in Hydrogen-bond Formation
VI — The Rôle of Hydrogen Bonds in Dyeing Processes — *C. H. Giles, D. S. E. Campbell, and D. Cathcart*

The Neutralisation of Acid-treated Wool by Solutions of Sodium Carbonate — *R. P. Harker*

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FORTHCOMING MEETINGS OF THE SOCIETY

Tuesday, 26th November 1957

NORTHERN IRELAND SECTION. *Terylene Polyester Fibre in the Linen Industry.* P. W. Eggleston, Esq., B.Sc., A.T.I. (Imperial Chemical Industries Ltd.). (Joint Meeting with the Textile Institute.) Kensington Hotel, **Belfast.** 7.30 p.m.

Thursday, 28th November 1957

WEST RIDING SECTION. *Problems in the Dyeing of Fast to Washing Colours on Wool Yarn.* J. F. Gaunt, Esq., Ph.D., F.R.I.C., F.T.I. (Patons & Baldwins Ltd.). Metropole Hotel, King Street, **Leeds.** 7.30 p.m.

Tuesday, 3rd December 1957

SCOTTISH JUNIOR BRANCH. *The Measurement of Damage to Wool Fibres.* J. C. Brown, Esq. (Clayton Dyestuffs Co. Ltd.). Technical College, **Paisley.** 7.30 p.m.

Friday, 6th December 1957

BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Fibro Blends.* W. Lonie, Esq., B.Sc., Ph.D. (British Rayon Research Association). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

LONDON SECTION. *Colour in Writing and Copying.* J. P. Gill, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Royal Society, Burlington House, **London W.1.** 6 p.m.

Tuesday, 10th December 1957

NORTHERN IRELAND SECTION. *An Impartial Observer's View of the Bleaching and Dyeing Industry—A Consultant Speaks Out.* T. L. Collyer, Esq., C.B.E., A.M.I.Mech.E., A.M.I.I.A. Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

SCOTTISH SECTION. *Dyeing of Acrilan.* H. R. Hadfield, Esq., M.Sc.Tech. (Imperial Chemical Industries Ltd.). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Recent developments in the dyeing of Acrilan will be reviewed and the dyeing and fastness properties of acid, chrome and disperse dyes will be detailed. The dyeing of Acrilan blends will be briefly reviewed.

Wednesday, 11th December 1957

MIDLANDS SECTION. *The Application of Amino Resin Finishes to Cotton.* A. R. Smith, Esq., B.Sc. King's Head Hotel, **Loughborough.** 7 p.m.

Thursday, 12th December 1957

MANCHESTER JUNIOR BRANCH. *The Textile Finisher.* F. Wood, Esq. Room C9, Manchester College of Technology, **Manchester.** 4.30 p.m.

WEST RIDING SECTION. *Watering of Acetate Poults.* E. France, Esq., B.Sc., A.R.C.S., A.M.C.T. (Courtaulds Ltd., Bocking). Victoria Hotel, **Bradford.** 7.30 p.m.

Tuesday, 17th December 1957

HUDDERSFIELD SECTION. *The Dyeing of Blends of Fibro with other Man-made Fibres and with Cotton.* W. Lonie, Esq., B.Sc., Ph.D. and R. A. Rutherford, Esq., B.Sc. (British Rayon Research Association). Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

Friday, 10th January 1958

LONDON SECTION. *Colour for the Dyer.* Professor W. D. Wright (Imperial College of Science and Technology). (Joint meeting with the London Section of the Oil and Colour Chemists' Association.) Royal Society, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 14th January 1958

NORTHERN IRELAND SECTION. *The Chemical Foundations of Fast Colour Printing.* A. S. Fern, Esq., B.Sc., D.I.C., F.S.D.C. (Imperial Chemical Industries Ltd.). Further details later.

Thursday, 16th January 1958

MANCHESTER JUNIOR BRANCH. *High Temperature Dyeing on Synthetic Fibres.* H. R. Hadfield, Esq., M.Sc.Tech. Room C9, Manchester College of Technology, **Manchester.** 4.30 p.m.

WEST RIDING SECTION. *Continuous Dyeing of Wool.* D. R. Lemin, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Victoria Hotel, **Bradford.** 7.30 p.m.

Friday, 17th January 1958

MANCHESTER SECTION. *The Chemical Foundations of Fast Colour Printing.* A. S. Fern, Esq., B.Sc., D.I.C., F.S.D.C. (Imperial Chemical Industries Ltd., Dyestuffs Division). The Textile Institute, 10 Blackfriars Street, **Manchester 3.** 7 p.m.

LONDON SECTION. Dinner and Dance. Waldorf Hotel, **London, W.C.2.**

Tuesday, 21st January 1958

HUDDERSFIELD SECTION. *Tests for Colour Vision.* F Jordinson, Esq, M.Sc., F.R.I.C., F.S.D.C. and T. Minshall, Esq., A.M.C.T., A.T.I. (Dyeing Department, Technical College, Huddersfield). (Joint Meeting with the Huddersfield Section, Royal Institute of Chemistry.) Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *Flame-resistant Finishes.* J. R. W. Perfect, Esq., B.Sc. (Bradford Dyers' Association Ltd.). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Developments with the use of phosphorus-containing resins.

Wednesday, 22nd January 1958

MIDLANDS SECTION. *Colloquium . . . Auxiliary products—Use and Abuse.* (Short papers by local members.) College of Technology, **Leicester.** 7 p.m.

SCOTTISH JUNIOR BRANCH. *Practical Aspects of Fastness Testing To-day.* P. R. Dawson, Esq. (Imperial Chemical Industries Ltd.). Technical College, **Paisley.** 7.30 p.m.

Friday, 24th January 1958

WEST RIDING SECTION. Ladies' Evening. Victoria Hotel, **Bradford.** 7.30 p.m.

Monday, 27th January 1958

BRADFORD JUNIOR BRANCH. *Spun-dyed Fibres, their Properties and Uses.* C. C. Wilcock, Esq., A.R.T.C., F.T.I., F.S.D.C. (Courtaulds Ltd.). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

Tuesday, 28th January 1958

LEEDS JUNIOR BRANCH. *Organic Pigments.* F. M. Smith, Esq., Ph.D. Department of Colour Chemistry and Dyeing, The University, **Leeds 2.** 3.15 p.m.

Thursday, 30th January 1958

WEST RIDING SECTION. *A New Approach to Pigment Dyeing of Piece Goods.* T. Weber, Esq. (Ciba Ltd., Basle). Victoria Hotel, **Bradford.** 7.30 p.m.

Saturday, 1st February 1958

MANCHESTER SECTION. Annual Dinner and Dance. The Grand Hotel, **Manchester.**

Monday, 3rd February 1958

HUDDERSFIELD SECTION. *Shrink Resistance of Wool.* A. N. Davidson, Esq., B.Sc. (Wool Industries Research Association). (Joint Lecture with the Huddersfield Textile Society.) Technical College, **Huddersfield.** 7.30 p.m.

Tuesday, 4th February 1958

LONDON SECTION. *Progress in Textile. A review of developments and their effect on industry and user—Dyeing and Finishing.* T. Vickerstaff, Esq., M.Sc., Ph.D., F.S.D.C. (Joint Meeting with the London Section, Textile Institute.) Chemical Society, Burlington House, **London, W.1.** 6.30 p.m.

continued on page xxxiii

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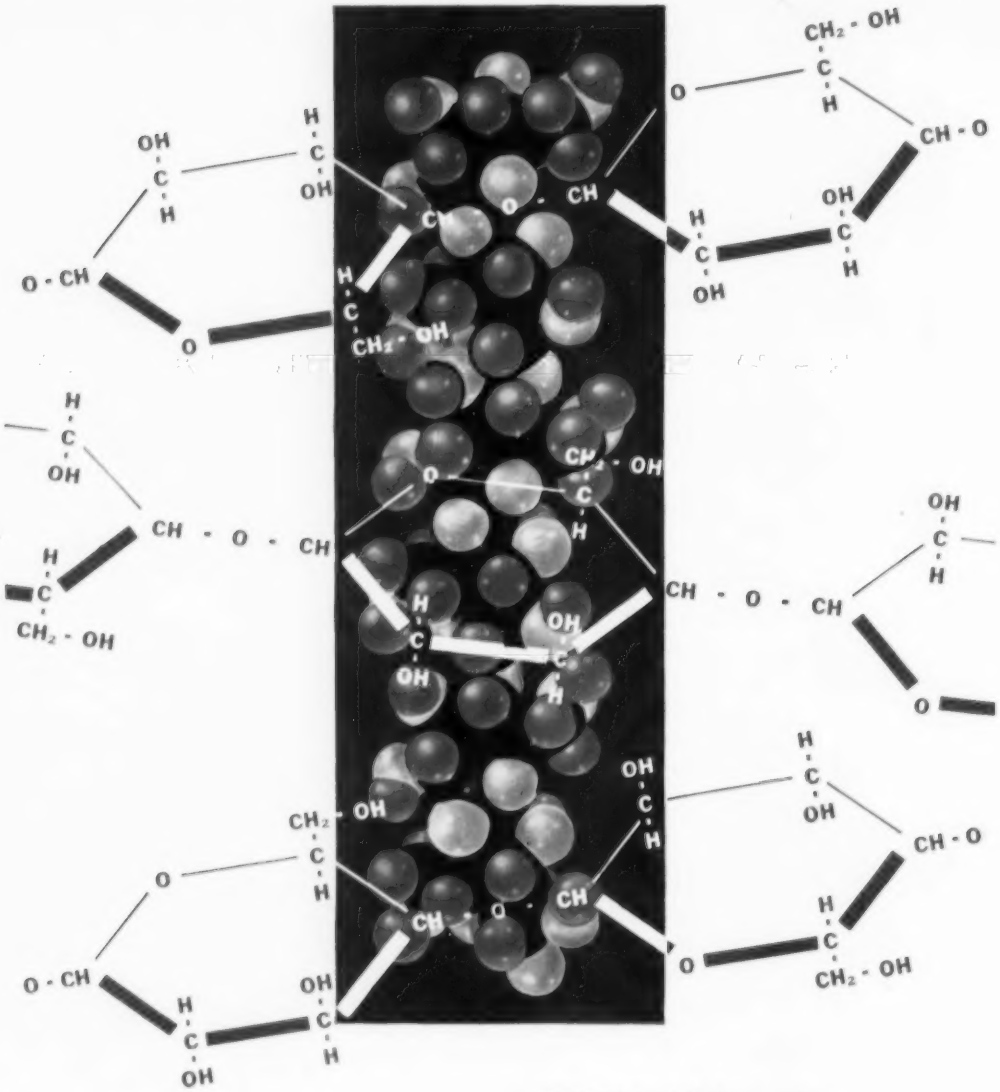

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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 73 Number 11 NOVEMBER 1957 *Issued Monthly*

Proceedings of the Society

The Supply, Treatment, and Disposal of Water in the Dyehouse

R. W. Richardson

Meeting of the Leeds Junior Branch held at the University, Leeds, on 5th February 1957, Mr. C. L. Bird in the chair

An attempt is made to review briefly the many aspects of water—its supply, treatment, and disposal—from the point of view of dyehouse management and the dyer, rather than from that of the water-treatment specialist.

We are continually reminded that the supply of water is a national problem, so that it is to be expected that an important user like the dyeing industry will be greatly affected. For special reasons the shortage of water may be even more acute in some cases.

It should be no more than restating the obvious to say that water is the most important of the dyer's raw materials, although recently we have heard something of more serious attempts to use non-aqueous systems. But is it so obvious? An adequate supply of clean soft water is too often taken for granted. Only in times of shortage or when the purification or effluent plant breaks down does management seem to realise its importance. Too often plant is expected to be run by operatives rejected from other parts of the works because of their low intelligence quotient, with occasional visits from exasperated technical staff from either the chemical suppliers or the equipment manufacturers. The technology of water treatment has advanced to keep pace with the exacting demands of dyers, only to fail in many cases at its point of application.

Many of the new developments in water technology were given impetus by the higher standards of fabric design produced for the mass market created by the man-made fibres. The requirements of high-pressure steam-raising equipment also gave rise to a very special need for high-quality water.

For some time the more enlightened local authorities have been pressing for better effluents from industry. This is particularly the case where wastes are discharged into streams from which water is being abstracted for domestic use. The problem has, however, never been treated as a national one or with any real urgency—perhaps, in some cases, fortunately for the dyehouse. With the passing of the Pollution (Rivers Boards) Act 1952, special powers were vested in newly constituted Rivers Boards to act more positively in their districts. Public attention, too, is continually focussed—usually by anglers—on the condition of our streams and rivers. The dyehouse effluent can be a serious offender in this matter, and the dyer can no longer sit back and expect inactivity to be on his side.

This paper is therefore conveniently divided into three parts—(i) supply, (ii) treatment, and (iii) disposal. With the first and last there are important statute and common law matters which arise, and these are discussed briefly, since they affect dyehouse management in no uncertain manner.

I—Sources of Supply

The extent of the problem here can be appreciated only by those either wishing to increase their usage of water or seeking sites for the building of new dyehouses. The problem is to a great extent hidden, since most dyehouses have been in existence for several decades, and were first sited to take advantage of water supplies existing at the time. The spread of towns and other industrial undertakings has in many cases absorbed any water originally surplus, and *riparian rights*, once almost taken for granted, are now worth hard cash. As far as rivers are concerned, all owners of adjacent land have the right to receive, and the duty to pass on, "pure" water—the riparian right. Well-owners are also protected in common law, to a certain extent, from poaching by sinking new wells into the same water-bearing strata close by.

Water supplies in this country may be divided broadly into three types, each having its particular advantages and disadvantages—

(i) South-east of the Cotswold escarpment, the principal supply is from wells sunk into either limestone or chalk. This water is usually very hard (20–50°), but it generally has the advantage of being of fairly constant composition (important in chemical dosing) and of good clarity. The hardness is largely temporary. In the chalk London basin the level of artesian wells is continually falling, whilst population and industrial development are increasing. The effective "capture areas"— the outcrops of the chalk— are also becoming smaller as they are built upon. The South Downs, in particular, are being more and more developed for housing, and the rain now runs to the rivers and sea in drainage systems instead of percolating into the chalk. London is now taking more and more Thames water to augment deep-well supplies.

(ii) In the Midlands, supplies may be from wells and rivers or piped from surface water in the Welsh hills and border country; the Severn is much used. Taking the area as a whole, these waters vary more in supply and composition than those in the South, and permanent hardness is more common in the deep wells.

(iii) In the North of England, Wales, and Scotland, supplies are mostly derived from surface water (run-off) collected by streams and stored in man-made dams and reservoirs. This water is usually much softer (often containing less than 5° hardness) than that in the rest of the country, but it is often coloured and contains suspended and colloidal matter. The low pH due to humic acids causes difficulties by its corrosive effect on iron mains, and this adds to the impurity present.

Few dyehouses are, therefore, situated so conveniently that some sort of purification is not ideally necessary, although some public supplies may be adequate. With the latter may come the problem of availability. Expansion of activities may be limited by the local authority's inability to meet new demands. Alternatively, the local authority may ask a higher price for water delivered above a certain volume.

II— Purification Treatments

The chief impurities in a water supply from the point of view of use for textile purposes are particulate and colloidal matter, colour, "hardness salts" and other interfering metal ions, acidity, and alkalinity. The disadvantages of the presence of particulate and colloidal matter in a dyehouse water supply are obvious, particularly when it is intended for package-dyeing. Colloidal iron from old mains, especially in areas of peaty, acid water, is the chief offender.

Calcium, magnesium, and iron are the most common hardness metals and they interfere by reacting to form insoluble salts with soaps, and insoluble complexes and untrue colours with dyes. Heavy metals, even in traces, can affect the colour of dyes and give deleterious catalytic effects, particularly in bleaching operations.

Excessive alkalinity or acidity makes control of dyeing difficult by influencing rates and equilibria. Organic matter, including cellulose itself, rapidly reduces many dyes in the presence of alkali at high temperatures. Little can be done with waters containing excessive amounts of dissolved solids: the cost of even partial deionisation would be prohibitive. This is not a serious problem, and is one which would arise only in special circumstances.

The supply of a satisfactory water for steam-raising is equally important for the dyer, and the introduction of higher-pressure equipment has meant a raising of quality. The efficient running and condition of boilers depend much on the quality of the water which they are using.

Clarification may be brought about by *ponding*, i.e. by allowing the particulate matter to settle. In many cases, however, the impurity is colloidal, and the rate of settling is virtually zero. It is then necessary to use a flocculating assistant, the most common being aluminium hydroxide produced *in situ* by adding an aluminium salt and adjusting the pH of the water to the appropriate value. The floc of aluminium hydroxide physically entraps and absorbs the impurity, and settles to give a clear supernatant. This is then filtered through graded sands and gravels.

The removal of colour presents special problems. In many cases flocculation will remove the greater part, but if this fails, active absorbents such as carbon and special aluminium silicates may be necessary. Resort to these measures suggests that the dyehouse has been wrongly sited, but even so the character of a water can change and make special treatment necessary.

The removal of ferrous iron also can be carried out in flocculating equipment after oxidising the iron by aeration to give ferric salts, which then precipitate as the hydroxide.

In softening, the aim should be to obtain a water of zero hardness. For many purposes this is unnecessary, or local conditions and economies may make it undesirable. Provided that the situation is appreciated and precautions are taken to use suitable sequestering agents, 1–2° of hardness may be tolerated. This level of hardness will be inevitable when softening is carried out by the lime–soda process. Base-exchangers can produce water of almost zero hardness.

The above figures are quoted in English degrees, i.e. expressed as grains of calcium carbonate per gallon. Although the use of *parts per million* (*p.p.m.*) is becoming increasingly common, it may require the introduction of the metric system in this country finally to get rid of this awkward expression. French units of hardness, calcium carbonate per hundred thousand, and parts per million are figures which are much easier to handle. The same criticisms apply in the expression of effluent analyses.

There are two main types of water-softening systems— ion exchange and chemical purification. Combinations of the two are now used in special cases.

ION EXCHANGE

The softening effect of some natural sands has been known for some time, and the use of these complex aluminosilicates in base-exchange reactions is well established. Commercial carbonaceous zeolites are now also being used in a similar way. The reaction between a hard water and the zeolite (Z) may be represented as follows—

$$\underset{\text{Insol.}}{xM^{2+} + Na_yZ} \rightleftharpoons \underset{\text{Insol.}}{M_xZ} + yNa^+$$

The reaction proceeds almost quantitatively to the right when bi- and ter-valent metals compete with univalent. In practice, water may be softened to 0·2° of hardness or less. When the zeolite has been converted to the hardness form, the reaction is reversed by treating with a concentrated solution of common salt. After *regeneration* in this way, the zeolite is washed and is ready for use again. The operator tests the treated water with soap or other suitable indicator (magneson reagent is rather better if magnesium hardness is present in the raw water) until the hardness breaks through. The cycle is then repeated. Automatic testing and regeneration equipment is now standard on the larger installations.

The cost of softening water by zeolite depends, of course, on the hardness of the raw water, which determines, for a given flow, the size of plant and the amount of regenerant salt needed. A large installation, delivering 50,000 gallons of soft water per hour, costs approximately £40,000–50,000. Taking depreciation, running costs, and chemicals into account, the operation will cost 9–12d. per thousand gallons. It is nevertheless an invaluable investment. An idea of the size of unit employed may be gauged from the fact that one cubic foot of zeolite will remove approx. 0·35 lb. of hardness (calculated as calcium carbonate) per regeneration, for which one-third to two-thirds of the bed volume of 10% common salt is required.

The use of ion-exchange resins, for the purification or complete deionisation of water for industry, is limited to special applications. In boiler-feed water for high-pressure systems, where the *make-up* is small, deionised water is used. The principles of deionisation with resins are now well known. The reactions involved may be represented as follows—

$$\underset{\substack{\text{Salt}\\\text{impurity}}}{MA} + \underset{\substack{\text{Sulphonic-}\\\text{acid resin}}}{R{\cdot}SO_3H} \rightarrow \underset{\text{Insoluble}}{R{\cdot}SO_3M} + HA$$

$$\underset{\text{Amino resin}}{HA + R'{\cdot}NH_2} \rightarrow \underset{\text{Insoluble}}{R'{\cdot}NH_2A}$$

CHEMICAL SOFTENING

Softening with a combined treatment of slaked lime and sodium carbonate is the only method used on a large scale. It has the advantage of removing bicarbonate and therefore gives a water which is less alkaline, or potentially so, than does zeolite softening. In order to precipitate all the calcium as carbonate, and magnesium as hydroxide, it can be shown that the lime dose must be equivalent to the total temporary (bicarbonate) hardness, plus *total* magnesium and dissolved carbon dioxide, and the soda ash dose equivalent to the permanent hardness.

Softening may be carried out either hot or cold and may be continuous or batchwise. The supernatant water from which the hardness salts have been precipitated is removed and filtered through graded sands and gravels. These particles become covered with carbonates and prevent, by seeding, the delivery of water supersaturated with calcium carbonate.

An excess of chemicals is, of course, required to complete the reactions, but it is important that this excess be kept to a minimum. Unnecessary solid matter should not be fed to the dyehouse or the boilers. In the latter case excess alkali can lead to a special type of metal fatigue known as *caustic embrittlement*. It is for this reason that lime–soda softening is essential for waters containing excess temporary hardness.

With boiler-feed water it is usual to add phosphate and special tannin extracts to the boiler drum direct, to prevent corrosion and scaling, which slowly occur even with the best waters. De-aeration also may be necessary at very high pressures. This may be carried out physically or chemically.

In the dyehouse, sequestering agents must be used to remove the last traces of the original hardness and any adventitious hardness. This is especially the case with lime–soda-softened water, which has a much higher residual hardness than that which has been zeolite-softened. The lime–soda process is also more difficult to control. The cost of lime–soda water must vary. A soft raw water may cost 9–12d. per thousand gallons, whilst a hard supply, e.g. from a chalk well, may cost more.

A combination of lime–soda and zeolite treatment has been proposed, but does not seem to have been taken up in practice on a large scale. A small excess of lime is added to precipitate temporary and magnesium hardness. The water is then passed through a bed of *carbonaceous* zeolite in the calcium form. This speeds up the reaction, filters off the precipitate, and *absorbs* excess lime. The remaining permanent hardness is then removed by conventional zeolite softening. The water obtained is very soft and contains little excess alkali, which is an important advantage over either of the two conventional methods.

For some years there have been marketed electrical devices which are claimed to prevent boiler-scale formation even with hard water. It is believed that the weak electric field applied prevents the growth of crystals adhering to the drums and to themselves, perhaps by modifying the crystal growth. Little concrete information is available on the process, and attempts to reproduce the effect in the laboratory have met with very limited success.

WATER ANALYSIS

Before leaving the subject of water purification, a brief word on water analysis will complete the picture. Both raw and treated water samples

must be tested as a routine in order that the correct chemical dose may be applied and its resulting effect checked. This may be done by titrating with acid to phenolphthalein and screened methyl orange end-points, from which the alkalinity and its type—bicarbonate, carbonate, or hydroxide—can be calculated. Total hardness was for years determined for control purposes by titrating with standard soap solution. The use of ethylenediaminetetra-acetic acid (E.D.T.A.), first proposed by Schwarzenbach, has much simplified this rather tedious method. Total hardness may be determined by titrating with standard E.D.T.A. solution using the dye Eriochrome Black T (C.I. Mordant Black 11). Calcium hardness alone (assuming other hardness to be due only to magnesium) may be similarly determined using murexide. From these results an approximate analysis of the water may be made by calculation.

In addition to these tests, it is usual to analyse the water in the boiler drums or tubes themselves to ensure that an adequate reserve of e.g. phosphate and a satisfactory residual alkalinity are present. It is useful also to test the *condensate return*, i.e. the water derived from steam condensed by enclosed heating coils and the turbines. Leakages in the system may be disclosed by an increase in electrical conductivity or chloride content.

III—Effluent and its Disposal

It is difficult to visualise the appearance our streams and rivers must have presented before the Industrial Revolution. Watercourses which are often no more than open sewers then supported game fish—now eels would find living conditions most uncongenial. Generally speaking, the natural history of the river and its banks is a very good guide to its pollution. Not only do the various species of fish, for example, react differently to the dissolved oxygen content of the water (itself a function of organic pollution), but the whole flora and fauna typify different conditions. By examination of quite small collections of river life, the biologist is able to learn the extent and the nature of the pollution. The asphyxial point for trout at 10°c. is approx. 1·5 p.p.m. of dissolved oxygen; for coarse fish this may be as low as 0·5 p.p.m. For fish to occupy a stream, at least twice the concentration of oxygen at the asphyxial point is required.

At a fixed ratio of effluent to river flow, the effect of a given polluting load depends on the character of the river itself. Slow, deep streams, where the rate of aerial oxygenation is small, become very much more affected than shallow, fast-flowing ones. The position at any point downstream from the outfall is determined, therefore, by the balance which results between the abstraction of oxygen by polluting materials and natural reoxygenation. The point of maximum polluting effect is thus not necessarily immediately downstream from the effluent outlet.

We, as a nation, have now reached the position where attempts to restore the character of our rivers to pre-industrial conditions are physically and economically impossible taking the short-term view. Riparian owners have in recent years, usually because of fishing interests, sought injunctions from the courts against the discharge of polluting liquors into the watercourse. In many cases, for the demands to be met in full would mean either capital expenditure beyond the means of the industry or closure of the works. Further, industry has been so concentrated that the standard of purity of any one effluent must be so high as to be virtually impossible to attain. In other words, it is unlikely that the river, when "polluted" with the best effluent practicable, could self-purify before reaching the next outfall downstream. The concentration of works along our rivers is therefore one of the major obstacles to the restoration of those rivers. The ratio of effluent to river flow is thus an important factor, and dry spells can undo years of patient work by all concerned.

The nation must be realistic in dealing with the problem, but being realistic does not excuse inactivity in the matter. Cooperation with Rivers Boards and local authorities usually benefits all the parties involved. In some cases the local authority is able to take an effluent into its drainage system at a reasonable cost, but in too many cases, unfortunately, the system is already overloaded.

Dyehouse effluents can be divided into three main types—those from wool, cotton, and mixed man-made fibre concerns. The differences in character are due mainly to the various preparatory processes carried out—wool scouring, cotton kiering, and mercerising, and man-made fibre desizing operations. Wastes include fibre impurities and breakdown products, sizes, detergents and soaps, dyes and chemical finishes. Of these, sizing materials, particularly starches and gelatin, are difficult to eliminate and at the same time are bad polluters. It is interesting to note that many of the newer sizing materials, e.g. carboxymethylcellulose and the acrylics, are less polluting from the deoxygenating aspect. In addition, there are acids, alkalis, and oxidising and reducing agents, of which hypochlorites, sulphides, and hydrosulphites are the worst offenders. In the main, however, the polluting effect of a textile waste is due to the high organic-matter content, which acts by depriving the stream of its dissolved oxygen.

The temperature of an effluent also has as important an effect as polluting waste itself. A rise in the temperature of a stream reduces its capacity to hold dissolved oxygen and at the same time increases the rate at which biological deoxygenation takes place. Fish require an approximately twofold increase in dissolved oxygen for every 10°c. rise in temperature.

The extensive use of "synthetic detergents" has brought many problems. Soap is relatively easy to remove. If sufficient hardness salts are not already present in the effluent, the addition of lime quickly precipitates calcium soaps, which can be removed. Other detergents survive this type of treatment, and no simple chemical methods will remove them. They are also highly resistant to oxidation by the micro-organisms on bacteria beds, and some may be actually bacteriostatic.

The presence of mountains of foam on most of our rivers shows the extent of this problem.

There are two well known systems of purification—chemical and bacteriological. They are often combined, since they are in many respects complementary in action. Since high local concentrations of inorganic and some organic substances can destroy the activity of "living" filter beds, it is important that an adequate mixing of the dyehouse effluent over a period is arranged. Where dyehouse wastes are discharged into domestic sewerage systems, this mixing may still be necessary if the ratio of industrial to domestic effluent is high. There are pros and cons in discharging into local authorities' mains. The cost to industry is usually very reasonable, but difficulties may arise when an expansion of activities becomes necessary. Too often both the mains and the treatment plant are just inadequate. It is not always sufficient to reduce the polluting "load" by, for example, a simple chemical flocculation, since the volume which the authorities' works has to deal with may still put the project out of court.

Chemical purification can be divided into the "neutralisation" of obnoxious materials and chemical clarification. In the first, treatment is designed to eliminate a particular substance, e.g. the neutralisation of acids, alkalis, and oxidising and reducing agents. Much mutual neutralising also takes place, especially in a mixed dyehouse. The cracking and extraction of wool fats is an example of a special preliminary separation. The elimination of reducing agents is, of course, particularly important, especially when these contain sulphur, in order to allow oxidation of the organic matter to proceed at a maximum rate and to avoid the formation of sulphide. When excessive amounts of reducing sulphur acids are discharged, the most effective means of removal is to treat the waste with chlorine, or more cheaply with waste hypochlorite bleaching liquors. When an effluent is discharged into a watercourse from which water is taken for domestic consumption, chlorination must not be carried out in the presence of tar acids, e.g. phenol and cresols used in the delustring of cellulose acetate. Chlorophenols are readily formed even in very dilute solution, and these can taint water, giving it a definite "antiseptic" flavour. These substituted phenols are highly resistant to bacterial oxidation, and can be detected in concentrations as low as one part in 10^9 of water. The works chemist must be constantly alert to the possibility of interactions of this sort, and when any change in the composition of the effluent occurs, all possible effects of this type must be considered.

The adjustment of pH to around the neutral point at an early stage is important and is best done by the addition of lime or acid.

Physical removal of coarse impurities may be carried out by ponding and by means of metal screens and filters. Chemical flocculation is the best approach when much colloidal material is present. Most textile wastes are of this type, since starch, gelatin, soap, and most dyes are colloidal in solution. The flocculation is carried out by adding copperas (crude ferrous sulphate), alumino-ferric (crude aluminium sulphate), or ferric salts (produced by the chlorination of copperas) at 0·1–0·3 g. of the hydrated salt per litre, and then adjusting the pH of the effluent to 9–10 with lime. The metal hydroxides precipitate as a coarse floc, which brings down with it most of the colloidal material, which it both entraps physically and adsorbs. After settling, the clear supernatant liquor is removed, either over the tank wall, or by using hollow floating arms. The process is usually continuous in operation until it is necessary to stop it in order to clean out the sludge, which is dewatered and dumped.

This process is capable of removing a significant proportion of the polluting load of most dyehouse effluents which might otherwise be placed on bacteria beds. Some local authorities may find it necessary to request a preliminary treatment of this sort before discharge to their sewers. Depending on the composition of the effluent, from 25% to 75% of the biological oxygen demand (B.O.D.) can be removed in this way.

Of the many tests proposed for the analysis and the classification of polluting liquids, the B.O.D. is now generally accepted as giving the best measure of polluting propensity. In effect, the test is designed to reproduce, in the laboratory, the changes which take place in the river. Briefly, it consists in incubating a sample of the effluent with clean aerated water and measuring the fall in dissolved oxygen content in a specified time. The results are expressed in grains of oxygen absorbed by one gallon of effluent (or in parts per 100,000). While the B.O.D. figure adequately describes the effluent, it need not be a complete measure of its effect on a river. As has been noted earlier, the rates of de- and re-oxygenation are important. The presence of substances which may inhibit bacterial oxidation can give a false picture of the amount of organic matter present, although this same inhibition may, of course, be taking place in the stream to which the effluent is discharged. The rate-determining factor for oxygen removal from the stream could be that of the removal of an inhibitor. In such cases the worst effects of pollution may be found well downstream from the outfall.

The B.O.D. cannot always predict the effect of the effluent on aquatic life. Where known poisons are present, supplementary tests must be carried out in order to determine the extent of their removal. There is a large area of uncertainty in interpreting these results because of the interplay of the poison and the oxygen content of the water. The asphyxial point is raised by toxic substances, or, to put it another way, the resistance of the fish is reduced in low-oxygen waters.

A simple test much used to give an indication of the oxidisable content of water is the oxygen absorption from acid permanganate solutions. In very few cases is it possible, however, to correlate this figure with the B.O.D. The amount of "albuminoid" ammonia also gives an indication of pollution, especially with wastes containing

proteins, and is therefore of most interest in connection with domestic wastes. Other tests (always including pH and temperature) depend on the special nature of the individual effluent. In determining trace impurities, the methods of ion exchange and chromatography are valuable analytical tools.

The second and more important purification system is the bacterial filter-bed, such as is used in most local-authority undertakings. Circular beds of graded coke and clinker are sprayed with the effluent, which percolates through and is subject to bacterial decomposition in the presence of oxygen. From the bottom, clear liquid is taken off from the small amount of solid matter (humus) which forms. All that is necessary is that the bed should be seeded with the appropriate organisms to promote what is in effect a large-scale B.O.D. experiment. With industrial wastes, inoculation is carried out with domestic sewage, and the bacteria are acclimatised to the waste with which they will have to deal, by slowly increasing its proportion in the liquors being applied.

The disadvantage of this method, as far as dyehouses are concerned, is the very large tank required for the polluting load usually encountered. Approximately 100 cubic feet of bed is needed to remove one pound of oxidisable matter per day. The effluent from a large mixed rayon dyehouse, for example, may be equivalent to that from a town of 20,000 people.

In the ideal dyehouse, much would be gained by having two drainage systems, one of which could be used for excessively polluting material. Once separated, it is often possible to culture a special filter-bed to receive a particularly bad waste, the liquors from which may then be disposed of by dilution with the remainder. Unfortunately, such a system would be very expensive to install in an existing dyehouse.

When bacterial filtration is used in conjunction with a chemical settling plant, an excellent effluent can be obtained, and this combination must be regarded as ideal. This is particularly so with dyehouse wastes, as the filter-bed seldom removes colour as efficiently as a chemical flocculation.

Where sufficient land is available, an important alternative to the use of filter-beds is that of "irrigation" methods. This involves the distribution of the waste over land as a shallow sheet of water, so that bacterial oxidation and decomposition by plant life can proceed as rapidly as possible. This method can give excellent results, particularly when the waste is pretreated chemically. Provided that the area is arranged so that maximum contact with air and soil is maintained, it needs little other attention. A resting period may be necessary after a time, and this is best arranged by drying-off areas in sections in rotation.

Special purification systems, such as that used for the recovery of wool greases, need to be determined for each case. Fortunately, a balanced dyehouse effluent is usually capable of being dealt with as a whole. Special cases usually involve nothing more than a high concentration of sulphide. Assistance and advice on all matters concerning the disposal of trade wastes can be obtained from the Water Pollution Research Laboratory, which has its headquarters at Stevenage, Hertfordshire.

Recovery of useful products from dyehouse effluents can be achieved in few cases in the textile trade. Wool grease is, perhaps, the only significant example. The commodity which is most wasted is, of course, heat. Here, again, it is extremely difficult to introduce any system of heat recovery into the older dyehouse. Since useful heat can be obtained only from the hotter effluents, it is necessary to have a dual system of drainage.

Finally, a word on economics. The cost of disposal of water depends so much on the nature of the wastes and the location of the dyehouse that it is impossible to give a figure. It could vary from almost nothing (apart from local rates) to perhaps 3s. 0d. per 1000 gallons where special treatment is required. A ferrous sulphate–lime treatment or a bacterial bed treatment would cost about 1s. 0d. per 1000 gallons. Treating effluent may, of course, become progressively more expensive as standards are tightened up.

* * *

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COVENTRY

(*MS. received 8th July 1957*)

Discussion

Dr. J. NIXON (*Yorkshire Ouse River Board*): I welcome the opportunity of explaining briefly some of the duties and obligations of the River Boards. The thirty-two River Boards, which cover practically the whole of England and Wales, were set up following the passing of the River Boards Act 1948, to co-ordinate under one authority for each watershed area the manifold duties of land drainage, pollution prevention, and maintenance of fishery interests, which duties had previously been carried out by separate authorities.

Prior to the passing of the above Act, a few River Boards had existed, being authorised under Private Acts of Parliament. One of the earliest was the West Riding of Yorkshire Rivers Board, set up in 1894, which administered for pollution-prevention purposes only the rivers and tributaries within the administrative area of the West Riding of Yorkshire. A serious difficulty existed in this political boundary to the Board's area, in that one main tributary rose in an adjacent county and had to be accepted at the county boundary in whatever condition it happened to be. This state of affairs is now altered, and the River Board has control over the whole river system of the Ouse from the source of each tributary down to the mouth at Apex Light.

The fact that the Yorkshire Ouse River Board took over the area previously administered by the long established West Riding Rivers Board gave it a good and sound start. The troubles and the antagonistic attitude of many manufacturers experienced by some of the new Boards had been met and smoothed out half a century earlier, and

in general the traders in Yorkshire now regard the River Board and its inspectors as an integral part of the industrial life of the county.

Long campaigning by three or four generations of inspectors has persuaded most traders that, although they are "riparian owners" by virtue of owning a riverside site, they do not own the river, and that other traders downstream have an equal right to enjoy the benefits of an unpolluted supply of water.

Co-operation between the Board's officers and industrialists is so close that it is doubtful whether any major expansion passes the planning stage without a joint meeting. This enables the industry to be fully aware in the early stages of any difficulties which are likely to arise in the field of effluent disposal, and to benefit from the accumulated experience of the Board's officers, which is freely available. Many new projects include a round 10% of capital investment for plant for treatment of trade effluents, and manufacturers have come to realise that the cost of treating the effluent to such a standard that it will not harm the river into which it is discharged is just as essential a charge as the buying of soap or soda-ash.

From a historic point of view it is rather interesting that Mr. J. H. Garner, later Chief Inspector of the West Riding Rivers Board, presented a paper to the Society in 1912 entitled *Treatment of Effluents from Dyehouses and Textile Factories*[1], for which he was awarded the Society's Silver Medal. It will thus be seen that the River Board's interest in your problem has stretched over a long number of years.

In my own personal experience, complaints by dyers of unsatisfactory river water have invariably been due to the discharge, upstream, of red cotton dye liquors by some other dyer. In one instance, the injured party, a commission dyer and finisher, threatened a Common Law action for damages (several pieces of black cloth with white stripes had finished black and pink) if only the culprit could be found. After weeks of careful searching, the offender was run to earth and all evidence for the prosecution obtained, including the dyeing of several cotton hanks by immersion in the river. Alas, on reporting all the facts to the injured party, the bubble burst: the offender was dyeing red pieces on commission for him. It would thus seem that the only safe cure is for all dyehouses along the river banks to have their effluent pipes upstream of their intake pipes!

To conclude on a more serious note, River Board officials are not just policemen but highly trained scientific officers, trying to keep the rivers of this country in such a good condition that the water is suitable for all normal trade purposes and thus to save heavy demands on domestic piped water supplies.

Reference

[1] Garner, J. H., J.S.D.C., **28**, 63, 110, 142, 179 (1912).

COMMUNICATIONS

Relative Stabilities of Metal Derivatives of *oo′*-Dihydroxyazo Dyes

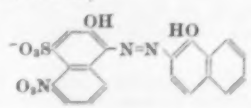
FRED A. SNAVELY, W. CONARD FERNELIUS, and BODIE E. DOUGLAS

The relative stabilities of metal derivatives of *oo′*-dihydroxyazo dyes (terdentate groups) have been measured potentiometrically in dioxan–water (75 : 25 by volume). The order of stability of the metal derivatives agrees with that already reported in the literature for monodentate and bidentate groups. The coordinating power of the diarylazo compounds for a given metal is proportional to the acid dissociation constants of the chelating agents. The one *o*-hydroxy-*o′*-carboxyazo dye which has been studied forms less stable metal derivatives than the *oo′*-dihydroxyazo dyes and differs from them in coordinating with beryllium.

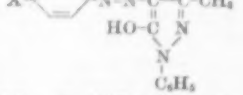
INTRODUCTION

The formation of metal derivatives by those azo dyes which contain hydroxyl, carboxyl, amino, etc. groups in one or more of the *ortho* positions has been studied in some detail[1]. Such compounds have found many applications in the dyeing of fabrics[1] and in the preparation of organic pigments[2].

While numerous tests have been made on the light fastness, resistance to laundering, etc. of the metal complexes, hardly any measurements have been made on the inherent stability of these compounds toward dissociation into their constituent ions. The first measurements of this type were those of Schwarzenbach and Biedermann[3] for the magnesium and calcium derivatives of dyes of the type of Eriochrome Black T (C.I. Mordant Black 11, C.I. 14645)—



The formation "constants" of the compounds formed by the metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} with a series of pyrazolone dyes—



(X = H, CH_3, Cl, NO_2) have been reported recently[4].

The work described here was undertaken to determine (1) whether the methods of potentiometric titration could be applied to coordinating ligands having two replaceable hydrogens and (2) the order of stability among a series of metals with a given dye and among a series of dyes with a given metal.

EXPERIMENTAL

Preparation of Materials

Each of the dyes was tested for purity by the use of a chromatographic column packed with

100–200-mesh Florosil*. Development of the chromatogram with dioxan showed only one band in each case. The neutral equivalents obtained by potentiometric titrations are given in Table I.

TABLE I

Neutral Equivalents of Various Dyes and their pK_{d1} Values

Dye	Neutral Equivalents		
	Calc.	Found	pK_{d1}
I	264·3	264	10·80
II	298·6	299	10·20
III	309·2	310	7·66
IV	394·4	393	9·60
V	294·3	296	10·66
VI	425·4	424	8·19
VII	256·3	256	6·83

I— 1 - (2 - Hydroxyphenylazo) - 2 - naphthol (CCC) was recrystallised from 95% ethanol.

II— 1 - (2 - Hydroxy - 5 - chlorophenylazo) - 2 - naphthol (DuP) was stated to be 99·6% pure.

III— 1 - (2 - Hydroxy - 5 - nitrophenylazo) - 2 - naphthol (DuP) was recrystallised from dioxan.

IV— 1 - (2 - Hydroxynaphthylazo) - 2 - naphthol - 4-sulphonic acid (C.I. Mordant Black 17, C.I. 15705) crystallised as the free acid when the sodium salt (CCC) was dissolved in 95% ethanol containing hydrochloric acid.

V— 1 - Phenyl - 3 - methyl - 4 - (2 - hydroxy - phenylazo)-5-pyrazolone (DuP) was crystallised from dioxan by addition of water.

VI— 1 - Phenyl - 3 - methyl - 4 - (2 - hydroxy - 4-sulphonaphthylazo)-5-pyrazolone (C.I. Mordant Red 7, C.I. 18760) (CCC) recrystallised from dioxan and concentrated hydrochloric acid.

VII— 2 - (2 - Hydroxy - 5 - methylphenylazo)-benzoic acid. *o*-Aminobenzoic acid (0·2 mole) was dissolved in 100 ml. of 95% ethanol; then 50 ml. of concentrated hydrochloric acid was added, and the solution cooled below 5°C. To the well stirred solution, which was sitting in an ice bath, 13·8 g. of sodium nitrite dissolved in as little water as possible was added dropwise. After the addition of the nitrite, urea was added until a negative test was obtained for nitrous acid with starch–iodide paper.

p-Cresol (24 ml., 0·25 mole) was dissolved in 1 litre of 50% ethanol and cooled to 5°C. The diazonium salt of *o*-aminobenzoic acid was rapidly added to the *p*-cresol solution. A concentrated solution of sodium carbonate was slowly added to the well stirred solution until evolution of carbon dioxide ceased. The deep red–orange solution was then allowed to stand for 8 hr. with occasional stirring.

The solution was then acidified with a considerable excess of hydrochloric acid. The red–orange precipitate was filtered, digested three times in hot water, filtered, and dried. The dye was recrystallised from benzene as red needles (yield 85%, m.p. 197–200°C.).

* Obtainable from the Floridon Co., Warren, Pa., U.S.A.

Potentiometric Titrations

The titrations were carried out in four-necked flasks immersed in a water-bath at 30·0 ± 0·1°C. A Beckman pH-meter (Model G) was employed, a calomel and either a regular* or a high-pH† glass electrode being used, the latter with a meter reading above 10·00. The flask was equipped with an adequate stirring device. All titrations at high hydroxyl ion concentrations and for such ions as iron(II), manganese(II), and cobalt(II) were carried out under nitrogen.

The solutions used were dioxan–water (75 : 25 by volume). Nitric acid (0·7412 N., 2 ml.) was added to each titration; in general, no more neutral electrolyte could be added without salting out the metal derivatives. Aqueous, carbonate-free 0·9983 N. sodium hydroxide was used throughout. The dioxan was purified by the Weissberger method[5] and stored over activated alumina; it gave negative tests for peroxides.

The dye (0·014 M. solution), metal ion, acid, and dioxan were carefully pipetted into the reaction vessel and equilibrated to a constant temperature and meter reading. In 100 ml. of solution were contained 0·70 millimole of dye, 1·482 millimole of nitric acid, and 0·210 millimole of metal nitrate. The standard solution of sodium hydroxide was added in increments of about 0·05 ml. to 0·10 ± 0·01 ml., and readings were taken on the pH-meter after each addition until a constant value was obtained. With this procedure results were found to be reproducible. The average time per titration was about 2–2½ hr. with the doubly charged metal ions.

In 75% dioxan it is necessary to calibrate the pH-meter. Van Uitert and Haas[6] have shown that the glass–calomel cell measures hydrogen ion activity as defined by the hydrogen electrode and that at a given salt concentration an empirical calibration holds over a range of meter readings, from 2 to 11.

The pH-meter was calibrated by titrating an aqueous solution of a measured amount of nitric acid with dioxan and taking readings on the meter. The values obtained in this fashion were checked against a titration of 75% aqueous dioxan with 0·1 N. nitric acid. The change in ionic strength throughout the titration and also the slight change in volume percentage can produce an error of ±0·03 in the correction factor. The correction used in this work was the addition of 0·40 to the reading of the pH-meter.

Preparation of the Nickel Derivative of Dye V

Dye V (0·012 mole), nickel chloride (0·004 mole), and sodium hydroxide (0·012 mole) were dissolved in dioxan (200 ml.), and boiled for 1 hr. The red microcrystalline powder which formed was filtered off, washed with dioxan, and dried in a vacuum desiccator. It did not melt below 300°C. (calc. for $Na_2Ni(C_{16}H_{12}O_2N_4)_2$ — C 55·76, H 3·51, N 16·26; found— C 56·34, H 3·70, N 16·0).

* 1190–80 glass electrode (Beckman Instruments Co.).
† 1190–75 glass electrode (Beckman Instruments Co.).

DISCUSSION

In the presentation of data on the stabilities of complex ions or neutral coordination compounds, it is customary to calculate formation constants. In the present case, if we represent the coordinating dye ion by Ch^{2-}, the reaction and formation "constant"* would be—

$$M^{2+} + Ch^{2-} \rightleftharpoons MCh$$

$$K_f = \frac{[MCh]}{[M^{2+}][Ch^{2-}]} \quad \text{(i)}$$

However, the actual equilibrium studied is—

$$M^{2+} + H_2Ch \rightleftharpoons MCh + 2H^+$$

$$K_{eq} = \frac{[MCh][H^+]^2}{[M^{2+}][H_2Ch]} \quad \text{(ii)}$$

and the calculation of K_f requires the independent determination of the dissociation constants of the dye—

$$H_2Ch \rightleftharpoons H^+ + HCh^-$$
$$HCh^- \rightleftharpoons H^+ + Ch^{2-}$$
$$K_{d1} = \frac{[H^+][HCh^-]}{[H_2Ch]}$$
$$K_{d2} = \frac{[H^+][Ch^{2-}]}{[HCh^-]} \quad \text{(iii)}$$

For the dyes studied, the first dissociation constants can be determined by simple potentiometric titration of the dyes in the absence of metal ions. However, the second dissociation is beyond the range of the pH-meter. Consequently, no formation constants can be calculated.

The expression (ii) for K_{eq} may be written—

$$K_{eq} = \frac{[MCh]}{[M^{2+}][Ch^{2-}]} \cdot \frac{[H^+]^2[Ch^{2-}]}{[H_2Ch]}$$
$$= K_f K_{d1} K_{d2} \quad \text{(iv)}$$

The question now arises whether it is possible to show the usual relation[7] between $\log K_f$ and pK_{d1} ($= -\log K_{d1}$) without knowing the actual magnitude of K_f. As long as the pH values measured in the titration, with a base, of a weak acid in the presence of a metal ion are less by a value of 2 than pK_{d1}, the ionisation of the weak acid will be so slight that effectively all of the Ch^{2-} will be combined either as MCh or as H_2Ch. Hence, one may use the expression—

$$K_{d\,1,2} = \frac{[H^+]^2[Ch^{2-}]}{[H_2Ch]} \quad \text{(v)}$$

whence—

$$\frac{K_{d\,1,2}}{[Ch^{2-}]} = \frac{[H^+]^2}{[H_2Ch]}$$

or—

$$p[Ch^{2-}] - pK_{d\,1,2} = p[H^2Ch] - 2pH \quad \text{(vi)}$$

The most widely used method for the calculation of formation constants is to plot $p[Ch^{2-}]$ against $\bar{n}$, the average number of bound chelate groups per metal ion or $[MCh]/[M^{2+}]_T$, where $[M^{2+}]_T$ is the total concentration of metal ion or the concentration at the beginning of the titration (making allowance for the amount of titrant solution added)[8]. If one plots not $p[Ch^{2-}]$, which cannot be determined, but $(p[Ch^{2-}] - pK_{d\,1,2})$ or its equivalent $(p[H_2Ch] - 2pH)$, which can be determined, one obtains the normal formation curve displaced by a constant amount $(-pK_{d\,1,2})$. Such plots permit many of the same comparisons as do true formation curves. At $\bar{n} = 0{\cdot}5$, $[MCh] = [M^{2+}]$ and equation (iv) becomes—

$$\log K_{eq} = p[Ch^{2-}] - pK_{d\,1,2} \quad \text{(vii)}$$

or—

$$\log K_f - pK_{d\,1,2} = p[Ch^{2-}] - pK_{d\,1,2} \quad \text{(viii)}$$

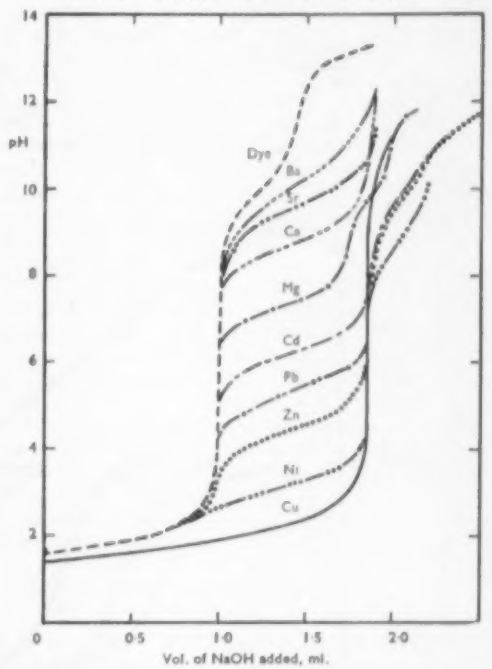


FIG. 1— Titration Curves of Dye II with Metal Nitrates

A representative set of titration curves is shown in Fig. 1 for dye II alone and with various metal ions. The buffer zones well below those of the neutralisation curve of the dye itself are the formation zones of the metal derivatives. The values for the first dissociation constant expressed as pK_{d1} are given in Table I. They were obtained by the customary mathematical and graphical methods. The first three dyes differ only in the nature of the substituent group. Their pK_{d1} values show a range of 3 logarithmic units and their strengths as acids are in the expected order— $NO_2 > Cl > H$.

In Fig. 2 and 3 the displaced formation curves are given for the metal derivatives of dyes I and V; those for the other dyes are similar. Table II records the values for $\log K_{eq}$. For each dye the order of stabilities for the metal derivatives is— $Cu^{2+} > Ni^{2+} (> Co^{2+}) > Zn^{2+} > Pb^{2+} > Cd^{2+} > (Mn^{2+}) > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The parentheses indicate that values for these ions are not available for all the dyes. This general order of stabilities is the same as that which has been noted for a wide variety of chelating agents[9]. Further plots of $\log K_{eq}$ against electronegativities[10] of the ions show the usual linear relation (Fig. 4).

The nickel ion gives clear evidence of forming complex ions of the type $NiCh_2^{2-}$, not only during

* The values presented in this paper are not true thermodynamic constants, since they have been calculated from concentrations rather than activities.

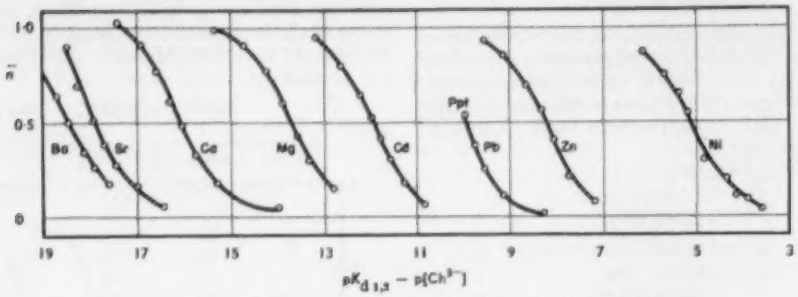


FIG. 2— Displaced Formation Curves for Dye I and Metal Nitrates

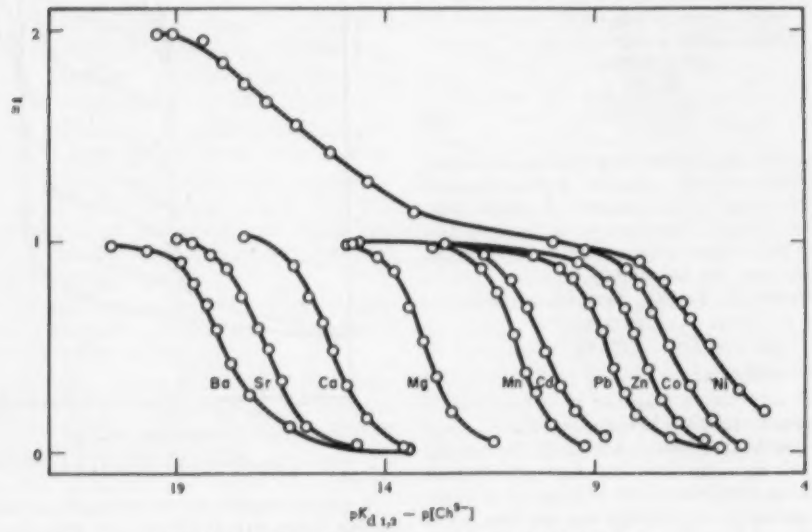


FIG. 3— Displaced Formation Curves for Dye V and Metal Nitrates

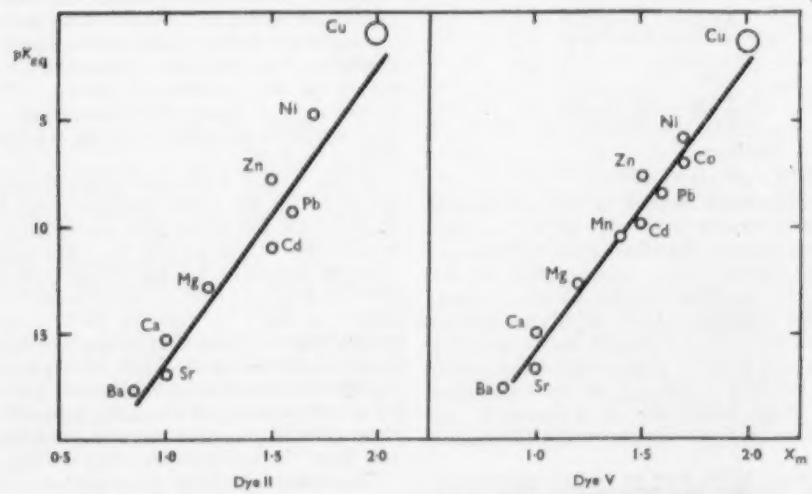


FIG. 4— Equilibrium Constants as a Function of the Electronegativities[10] of the Metal Ions

TABLE II

Stabilities of Complexes of Dyes with Metal Ions

($-\log K_{eq}$ or ($pK_{d\ 1,2} - pCh^{3-}$) values)

Dye ...	I	II	III	IV	V	VI	VII
Cu^{2+}	~1·4	~1·2	~1·0	~1·4	~1·4	~1·0	~1·5
Be^{2+}	—	—	—	—	—	—	3·8
Ni^{2+}	5·1	4·9	3·7	4·6	5·9	4·6	6·4
Co^{2+}	—	—	—	—	7·1	5·8	7·3
Zn^{2+}	8·2	7·8	6·1	7·9	7·6	6·4	8·0
Pb^{2+}	10·1	9·3	7·8	9·3	8·5	8·3	8·2
Cd^{2+}	11·9	11·0	9·4	11·6	10·0	9·8	9·8
Mn^{2+}	—	—	—	—	10·6	9·8	10·6
Mg^{2+}	13·7	12·9	10·9	12·8	12·8	12·0	~12·6
Ca^{2+}	16·1	15·4	13·2	~15·0	15·0	~14·5	—
Sr^{2+}	~17·9	~17·0	~16·7	—	16·7	—	—
Ba^{2+}	~18·5	~17·6	—	—	17·6	—	—
Ni^{2+}*	18·1	16·6	13·2	16·7	15·5	13·8	12·3

* Values of log K_{eq} for the reaction— $NiCh + H_2Ch \rightleftharpoons NiCh_2^{2-} + 2H^+$

titration, but also by yielding a sodium nickel salt of dye V, which can be isolated. In the titrations of Fe^{2+}, Co^{2+}, and Mn^{2+}, three protons were neutralised per metal ion. However, for dyes V–VII with Co^{2+}, the third proton could be titrated only after standing for several hours. Hence, equilibrium constants for Co^{3+} could be calculated. For these same dyes and Mn^{2+}, the bivalent state appeared to be stabilised.

A few titrations have been carried out with iron(III), aluminium(III), and chromium(III). They all coordinate very strongly but, with the exception of iron(III), the titrations are quite slow. For example, the chromium runs required hours between additions of base. The approximate order of stability, as shown by the few runs made, is Fe > Cr > Al.

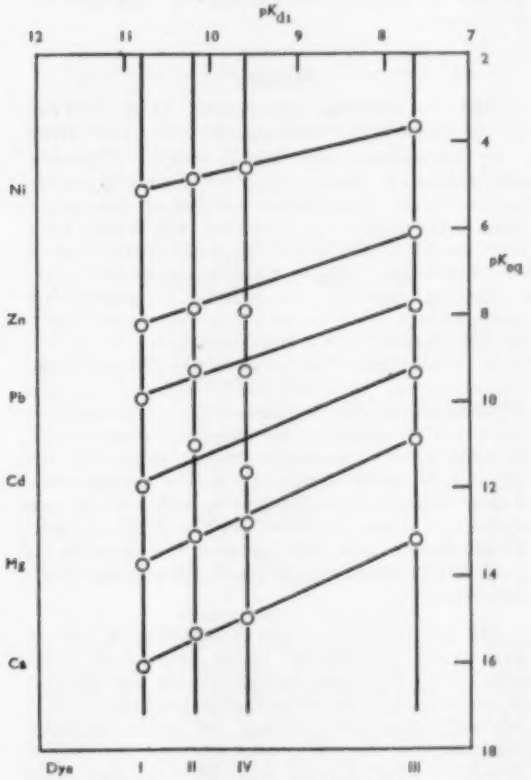


FIG. 5— Equilibrium Constant ($-\log K_{eq}$) as a Function of Acid Dissociation Constant (pK_{d1})

In Fig. 5 values for log K_{eq} of the metal complexes of the *oo'*-bishydroxyarylazo compounds have been plotted against the first acid dissociation constant of the dyes. A linear relationship is noted in all cases, so that the nitro-substituted compound (the strongest acid) forms the weakest complex, while the H-substituted dye (the weakest acid) forms the strongest complex with a given metal ion*. Although dye IV has a different type of charge, it follows these linear relationships. If a sufficient number of pyrazolone dyes were measured, they would probably give similar lines but of different slopes.

When the *o*-hydroxy-*o'*-carboxyazo dye is compared with the *oo'*-dihydroxyazo dye, it is found that, as would be expected, the first acid dissociation constant is much higher. From this one predicts and finds for the metal derivatives a lower order of stability. However, beryllium, which showed no tendency to coordinate with the other dyes, does so strongly with this type and falls between copper and nickel in the stability series. Apparently, the two oxygen atoms in an *oo'*-dihydroxy compound cannot approach sufficiently close together to bond the small beryllium ion, whereas there is no such limitation in the *o*-hydroxy-*o'*-carboxy compounds.

* * *

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* On first consideration the converse of this statement may appear to be the correct one. The confusion is resolved when one considers the sign of the value for log K_{eq}. Since log K_{eq} = log K_f − $pK_{1,2}$ and numerically the value of $pK_{1,2}$ is greater than that of log K_f, the values of log K_{eq} are negative, so that the larger the value of log K_{eq} (as long as the sign is negative) the less is the value of log K_f.

The Preparation and Properties of Regenerated Cellulose containing Vinyl Polymers
III— Moisture Relations

G. LANDELLS, J. A. LEATHLEY, and C. S. WHEWELL

Large quantities of hydrophobic vinyl polymers deposited inside viscose rayon fibres reduce water imbibition comparatively slightly, but hydrophilic polymers increase the imbibition. Measurements of the absorption–desorption isotherms of fibres containing various polymers show that deposition of polymethyl methacrylate or polystyrene produces little effect on the moisture contents calculated on the weight of cellulose. Introduction of hydrophilic polymers increases the moisture contents of the fibres.

Introduction

In Part I [1] of the present series of papers methods were given for depositing vinyl polymers inside viscose rayon filaments. In Part II [2] the location of the polymers with respect to the filament was confirmed by staining and swelling tests, and the effect of the polymers on certain physical properties, in particular stiffness, was studied. The present paper deals with the effect of internally deposited vinyl polymers on the moisture absorption properties of viscose rayon. It is well established that condensation resins of the urea–formaldehyde and melamine–formaldehyde type when applied as precondensates of low molecular weight penetrate cellulosic fibres and are hardened in the internal structure of the fibres. Now, many vinyl polymers possess the properties of hardness and water resistance, which would appear to make their formation inside textile fibres of special interest from both technical and purely scientific points of view. To study the effect of the internal deposits on absorption of moisture, measurements have been made of (*a*) imbibition of liquid water and (*b*) the amount of moisture taken up at equilibrium from atmospheres of known relative humidity using samples of viscose rayon containing various amounts of vinyl polymers. The results obtained have been compared with those of samples treated with formaldehyde and with those containing urea–formaldehyde resin.

Experimental

1. MATERIALS

Viscose rayon yarn (Courtaulds Ltd.) of 980 denier, 178 filaments was used. Except where otherwise stated, vinyl polymers were deposited in the various samples by the methods described previously [1].

2. METHODS

(*a*) *Determination of Water of Imbibition*

The samples (0·3 g. dry weight) were wetted-out in distilled water for 12–16 hr. at room temperature and lightly squeezed before being centrifuged. They were then placed in tubes so that the samples rested on constrictions placed 1 in. from the bottom of the tubes. The tubes were centrifuged, the time recorded being that which elapsed between switching the centrifuge on and switching it off. To prevent loss of moisture by evaporation, the tubes were corked during the centrifuging, and the specimens were afterwards transferred to tared weighing bottles and weighed immediately. Some of the samples were centrifuged at 1800 r.p.m. (363 ***g***), but most were centrifuged at 3000 r.p.m. at a radius corresponding to 1000 ***g***. Preliminary results showed that the amount of water removed by the above method reached a limiting value after centrifuging for 5 min. All figures for water of imbibition, except where otherwise stated, are calculated on the basis of the weight of dry cellulose in the sample.

(*b*) *Absorption–Desorption Isotherms*

These isotherms were determined by the usual methods. For conditioned weights the samples were allowed to remain in tared weighing bottles in atmospheres of various relative humidities maintained by means of mixtures of sulphuric acid and water. The dry weights were determined by drying the sample over phosphorus pentoxide for 2–3 weeks.

Results

SERIES I— REMOVAL OF WATER FROM VISCOSE RAYON CONTAINING VARIOUS AMOUNTS OF POLYMER

In this series of experiments samples of treated and untreated viscose rayon were centrifuged for various times, a sufficient number of determinations being made to ensure that the results were reproducible and accurate. Typical results obtained on untreated viscose rayon, viscose rayon containing various percentages of polymethyl methacrylate, and viscose rayon containing 15·9% of urea–formaldehyde resin are shown in Fig. 1. It is evident that the water of imbibition of the viscose rayon is considerably reduced by the deposition of methyl methacrylate. The extent of reduction is, however, less than that produced by deposition of urea–formaldehyde resin. If the amount of water remaining in the sample after 5 min. centrifuging is plotted against the polymer content, a smooth curve (see Fig. 2) is obtained which shows that the greater the amount of polymethyl methacrylate present the lower is the imbibition.

All the imbibition–time-of-centrifuging curves show a rapid initial fall in the amount of water retained by the fibres during the first few minutes of centrifuging. As centrifuging proceeds, this is followed by a further steady fall in the moisture content, and the differences between the values obtained after 5 min. and 20 min. are small compared with the difference between the values for samples containing various amounts of polymer.

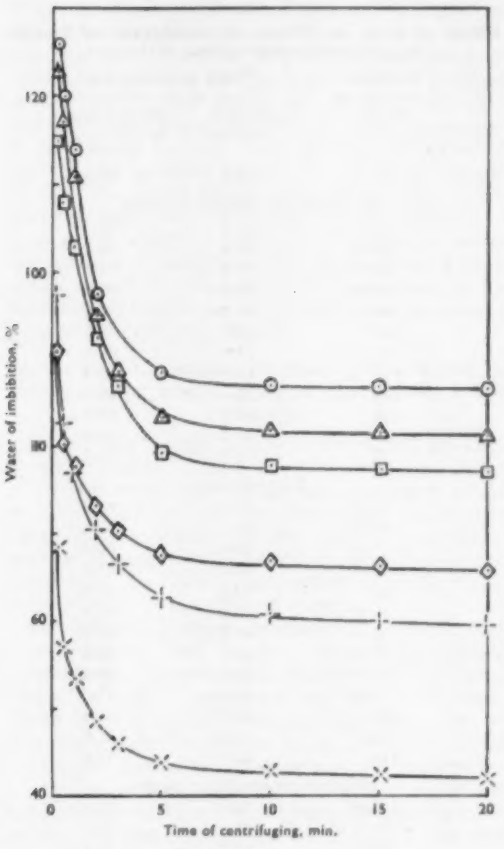

FIG. 1— Effect of Time of Centrifuging at 1000 *g* on Water of Imbibition of Viscose Rayon containing Polymers

SERIES II— THE WATER OF IMBIBITION OF VISCOSE RAYON CONTAINING DIFFERENT PERCENTAGES OF VARIOUS POLYMERS

The values obtained for the water of imbibition of untreated viscose rayon and viscose rayon containing polymethyl methacrylate, polystyrene, polymethacrylic acid, polymethacrylamide, and polyacrylonitrile after centrifuging for 5 min. at 1000 *g* are illustrated in Fig. 2. It is convenient to discuss the results obtained for hydrophobic polymers and hydrophilic polymers separately.

Hydrophobic Polymers

The data indicate that incorporation of polymethyl methacrylate, polystyrene, or polyacrylonitrile reduces the imbibition, the effectiveness increasing with the amount of polymer deposited. The lowest values obtained are 60% for a sample containing 130% of polymethyl methacrylate, 43% for one containing 118% of polystyrene, and 49% for one containing 109% of polyacrylonitrile. The reduction in the imbibition is in no case, however, so great as that caused by depositing only 15·9% of urea–formaldehyde resin. The vinyl polymer–fibre system differs greatly from the urea–formaldehyde–fibre system. For example, when vinyl polymers

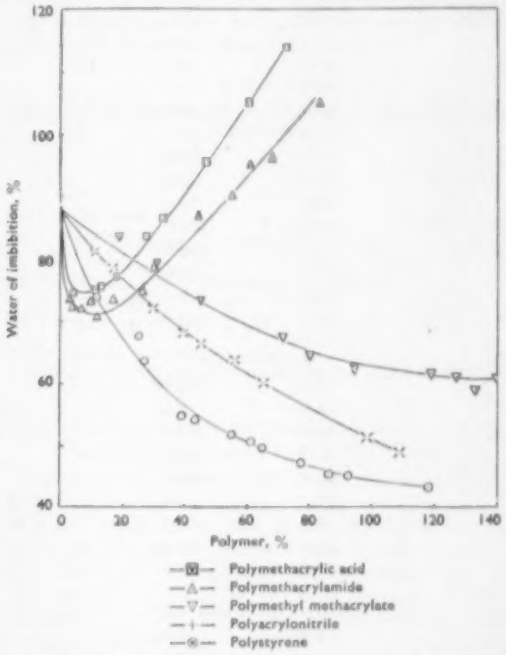

FIG. 2— Water of Imbibition of Viscose Rayon containing Vinyl Polymers

are deposited in the fibre, the polymerisation takes place when the fibre is fully swollen; whereas resin formation in the case of urea–formaldehyde resins takes place mainly during baking, when the fibre is dry and shrunken. Deposition of the vinyl resin causes the fibre to increase considerably in diameter (see Table I), whereas internal formation of urea–formaldehyde resin causes comparatively little change in the diameters of the fibres. Another marked difference between the two systems is the possibility of cross-linking during the formation of urea–formaldehyde resins. No such cross-linking would be likely with vinyl resins. It would appear, therefore, that the greater effectiveness of the urea–formaldehyde treatment is due to resin formation and the possibility of cross-linking while the fibre is in a non-swollen state.

Hydrophilic Polymers

If the water of imbibition of viscose rayon containing polymethacrylic acid is expressed as a percentage of the total weight of polymer and rayon, it is reduced to about 65% by the deposition of 20% of polymer. Deposition of more than 20% of polymer causes a further reduction, and there is subsequently a linear relation between the amount of polymer and the water of imbibition. When results are expressed as a percentage of the weight of dry viscose rayon, the presence of small amounts

TABLE I

Diameter of Viscose Rayon containing Various Amounts of Polymers

Polymer (% on wt. of fibre)	Increase in (diameter)^2 (%)
POLYMETHYL METHACRYLATE	
2·46	−1·0
7·19	8·68
17·3	15·8
18·9	10·2
31·6	30·4
34·3	32·7
45·2	26·5
71·6	60·0
94·2	76·9
109·0	110·0
119·0	126·0
128·0	119·0
141·0	120·0
154·0	155·0
POLYSTYRENE	
5·28	2·77
9·50	9·10
15·5	19·8
25·2	32·5
26·8	38·8
35·0	52·6
48·2	72·4
61·9	91·5
67·0	98·0
POLYMETHACRYLIC ACID	
4·05	2·96
9·40	11·7
13·0	12·4
17·8	19·6
26·5	23·6
33·7	33·4
47·0	57·6
60·5	64·6
POLYMETHACRYLAMIDE	
6·70	4·43
9·90	7·02
11·9	16·3
17·0	20·3
26·4	27·7
29·9	36·5
44·6	49·8
49·5	63·5
61·0	65·0
68·0	87·4
POLYACRYLONITRILE	
11·2	4·62
17·0	11·5
27·8	24·6
39·5	43·4
45·7	47·5
56·1	60·5
65·2	59·3
75·3	84·7
UREA–FORMALDEHYDE RESIN	
18·6	8·0

TABLE II

Effect of Heat on Water of Imbibition of Viscose Rayon containing various Polymers

Polymer (% on wt. of fibre)	Water of Imbibition (% on wt. of cellulose) Before heating	After heating at 150°c. for 15 min.
—	88·3	82·3
POLYMETHYL METHACRYLATE		
18·9	83·4	77·0
31·6	79·4	79·4
45·2	73·5	67·5
71·6	67·5	62·0
80·1	64·3	59·0
94·2	62·5	57·5
119	61·5	55·0
127	60·9	54·3
133	58·8	54·0
140	60·7	53·6
141	60·3	53·0
154	61·2	53·2
POLYSTYRENE		
11·7	74·8	67·2
25·2	67·5	61·5
27·3	63·4	56·5
39·5	54·8	51·5
43·6	54·0	48·8
55·6	51·8	47·5
61·3	50·5	45·5
61·9	49·7	44·8
65·0	49·5	43·4
77·2	47·0	43·0
86·1	45·2	41·4
92·1	45·0	41·0
118	43·0	37·8
POLYMETHACRYLIC ACID		
4·05	74·5	71·4
11·5	75·0	74·7
13·0	75·7	73·5
18·0	77·0	74·5
27·8	83·5	80·0
32·4	86·5	83·0
47·0	95·5	93·0
60·5	105·0	99·4
72·5	114·0	110·0
POLYMETHACRYLAMIDE		
2·85	73·5	75·3
3·80	72·0	77·3
6·70	72·0	77·5
9·90	73·0	79·5
11·9	70·5	78·9
17·0	73·4	80·8
26·4	74·7	83·7
29·9	78·5	88·5
44·6	86·8	98·6
55·2	90·0	107·0
61·0	95·0	109·0
68·0	96·0	113·0
83·8	105·0	123·0
POLYACRYLONITRILE		
11·2	81·0	79·9
17·0	78·4	77·1
30·0	72·0	70·1
39·5	68·0	64·8
45·7	66·3	63·8
56·1	63·8	62·0
65·2	60·0	57·5
75·3	58·7	56·0
98·6	51·0	49·2
109	48·9	46·9

of polymethacrylic acid causes a reduction in the imbibition, the minimum value corresponding to about 8% of polymer. Larger amounts of polymer increase the value, the relation between amount of polymer and water of imbibition being approximately linear (see Fig. 2). 35% of polymer is required to increase the water of imbibition of the treated material to that of untreated viscose rayon. The initial decrease in the capacity of the fibres to hold water is possibly due to blocking of sites which would normally be available for water combination or to reduction of the number of voids within the fibre. Similar results are obtained for the water of imbibition of viscose rayon containing polymethacrylamide (Fig. 2).

SERIES III— THE EFFECT OF HEAT ON THE WATER OF IMBIBITION OF VISCOSE RAYON CONTAINING VINYL POLYMERS

Since many vinyl polymers soften on heating, it was considered possible that the imbibition of viscose rayon containing vinyl polymers would be altered by heating, as this might induce the formation of a continuous film. Samples containing various monomers were, therefore, heated at 150°C. for 15 min., and determinations made of the water of imbibition of the treated samples.

The results obtained are shown in Table II, and it is evident that heating samples containing hydrophobic polymers or polymethacrylic acid causes a small reduction in the imbibition. There is, however, no evidence that this is due to physical changes in the polymer, for the water of imbibition of untreated viscose rayon is reduced by a similar amount on heating. The water of imbibition of fibres containing poylmethacrylamide polymers is increased by heating. It is not easy to explain this observation, but it is possible that heating may break down the polymer. It was found that viscose rayon containing polymethacrylamide does not respond so easily to treatment with acidic formaldehyde as does untreated viscose rayon. This is evident from Table III, in which values are given for the water of imbibition of the two materials after being immersed in 20% formaldehyde in presence of 0·3% ammonium persulphate and then dried and baked at 110°C. for 15 min. This is undoubtedly primarily due to the failure of the formaldehyde to react, perhaps because the internal pH of the system is too high, but, as shown by the figures given in Table II, an *increase* in imbibition of some 17% is brought about when viscose rayon containing 55% of polymethacrylamide is heated in air at 150°C. for 15 min. Any reduction in imbibition which heating with formaldehyde might effect would also have to offset this increase.

TABLE III

Effect of Formaldehyde on Viscose Rayon containing Polymers

	Material	Water of Imbibition (%)*
(1)	Untreated	101·5
(2)	Viscose rayon treated with acid–CH_2O†	38·4
(3)	Viscose rayon containing 55% of polymethacrylamide	112·0
(4)	Treated with acid–CH_2O	117·0

* Measurements made at 363 *g*.

† Reagent used: 20% CH_2O containing 0·3% ammonium persulphate. Time of heating at 110°C. 15 min.

ABSORPTION–DESORPTION ISOTHERMS FROM VISCOSE RAYON CONTAINING VINYL POLYMERS

The results obtained are summarised in Table IV.

It is evident from these data that deposition of polymethyl methacrylate and polystyrene produces little effect on the moisture contents calculated on the weight of cellulose in each sample. When calculated on the total weight of polymer and cellulose the moisture content is, of course, low, and decreases as the percentage of polymer in the sample increases. The moisture contents of samples containing hydrophobic vinyl polymers are thus similar to those of viscose rayon containing urea–formaldehyde resins (see Table IV). These results would suggest that the deposition of resins does not reduce the number of sites available for combination with water.

It is possible that deposition of vinyl polymers is in effect the laying down of a polymer lattice on the lattice of cellulose. The two interpenetrating lattices will have different restraining effects, and this is reflected in the solubility characteristics of

TABLE IV

Moisture Contents (%)* of Viscose Rayon containing Polymers

Polymer (% on wt. of fibre)		Absorption 10% R.H.	26% R.H.	41% R.H.	62% R.H.	82% R.H.	90% R.H.	Desorption 10% R.H.	27% R.H.	42% R.H.	63% R.H.	82% R.H.	90% R.H.
No polymer ...	—	5·22	7·8	10·2	14·8	21·2	25·5	5·63	8·76	12·0	16·4	23·9	27·8
Polymethyl methacrylate	59·3	5·15	15·5	17·7	22·8	25·8	29·0	59·8	10·0	13·7	19·4	28·5	33·0
	114	5·63	11·7	14·2	18·9	27·2	30·3	6·34	10·0	14·1	21·0	31·4	36·0
Polystyrene ...	48·2	5·13	8·9	11·1	15·4	21·8	25·6	5·38	8·30	11·5	15·9	23·6	27·7
	118	4·44	9·3	12·3	16·4	21·6	24·7	7·00	10·0	15·0	21·2	31·1	35·4
Polymethacrylic acid	60·7	8·35	13·2	16·9	24·3	35·6	40·4	9·44	15·8	21·6	29·4	43·2	47·5
	109	11·5	19·3	22·6	33·5	49·5	56·9	12·4	20·2	28·4	40·3	60·0	66·6
Polymethacrylamide	55·2	10·8	18·1	22·7	31·9	44·5	50·5	11·8	18·5	25·2	34·2	47·7	51·7
	138	19·6	27·2	34·8	48·9	73·0	83·7	21·6	34·7	46·9	62·0	88·0	95·7
Urea–formaldehyde resin	15·8	5·64	9·53	11·3	15·2	21·5	25·8	6·22	9·97	13·2	17·6	24·1	27·4
	16·8	5·06	8·85	11·2	15·5	21·6	26·0	6·30	10·2	13·4	17·7	24·6	28·1

* Calculated on weight of dry cellulose.

viscose rayon containing vinyl polymers. The new lattice acts as a restraining system, and so prevents complete dissolution in cuprammonium hydroxide. In a similar way, the water of imbibition of viscose rayon containing hydrophobic polymers is reduced. On the other hand, the moisture contents, especially at relative humidities below 90%, are comparatively unaffected. This would be expected, as deposition of the polymers does not affect the number of active points available for absorption of moisture. The data obtained for viscose rayon containing urea–formaldehyde resins would suggest that perhaps a similar mechanism is important in determining the properties of these materials, for again the change in moisture contents at relative humidities less than 90% is not great, but the changes in both water of imbibition and solubility in cuprammonium hydroxide are considerable. When hydrophilic polymers are introduced into viscose rayon, the moisture contents appear to be additive, each polymer making its own contribution.

* * *

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The Swelling and Solution of Synthetic Fibre-forming Polar Polymers in Liquids*

W. R. MOORE

The general principles governing the interaction of organic liquids and synthetic fibre-forming polymers (including cellulose acetate) are considered, and the factors which determine whether a liquid will dissolve or swell a given polymer are discussed.

INTRODUCTION

Many processes in the manufacture and finishing of a synthetic fibre-forming polar polymer entail treatment of the polymer with an organic liquid. It may, for example, be necessary to dissolve the polymer in order to spin it from solution or to determine its molecular weight. Finishing processes may involve treatment of the polymer with organic liquids alone or in solution. Organic liquids may be used as dyeing assistants, and in such cases it is probable that the liquid swells or plasticises the polymer. The factors which determine whether a liquid will dissolve or swell a given polymer and which govern the degree of swelling or solvent action are clearly important. The aim of this paper is to consider some of the general principles governing the interaction of organic liquids and such fibre-forming synthetic polymers as the polyamides (nylons, Perlons), polyethylene glycol terephthalate (Terylene—ICI), polyvinyls (Orlon—DuP), and polyvinylidene chloride (saran). Such principles are then applied to some specific cases of polymer–liquid interaction. Cellulose acetate is included under synthetic fibre-forming polar polymers. Although many of the principles apply also to natural fibrous polymers, these are not included, since consideration of their interaction with liquids often requires special treatment.

POLYMER–LIQUID INTERACTION

For any mixing process, such as swelling or solution, to occur, the Gibbs free energy G of the whole polymer–liquid system must decrease; i.e. the change in free energy ΔG must be negative. The concept of free energy was considered in an earlier paper [1], which showed that the absorption of dyes by wool is accompanied by a decrease in free energy. In a similar way G must decrease if polymer and liquid mix, either to a limited extent (as in swelling) or completely (as in dissolution). It was also pointed out [2] that the free energy change can be represented as made up of heat and entropy changes, according to the equation—

$$\Delta G = \Delta H - T\Delta S \qquad \text{(i)}$$

where ΔH is the heat change in the process considered, ΔS the entropy change, and T the absolute temperature. It is clear that whether the polymer and liquid mix or not depends on the balance of the heat change, the entropy change, and the temperature. Increasing the temperature will generally favour mixing, since it will tend to decrease ΔG if ΔS is positive, as it must be for simple mixing (see below).

The Entropy Change

Entropy is a measure of randomness or disorder. It is also dependent on the freedom of motion of the molecules considered. If a molecule is restricted so that it can move in only a limited way, e.g. a dye molecule in a particle of solid dye, it will have a limited entropy. On the other hand, a dye molecule in solution will have much greater freedom of movement and randomness of position, and consequently a greater entropy. Mixing processes tend to produce conditions under which the

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molecules have greater randomness of arrangement and freedom of motion. They lead, therefore, to an increase in entropy; i.e. ΔS is positive. In a solid particle of polymer, or in a fibre, the very large polymer molecules are effectively fixed in position. If mixed with a liquid to form swollen polymer or a solution, the polymer molecules are free to move not only in position but also by the flexing or coiling of individual chain molecules. This increased freedom of motion leads to a large increase in entropy when a polymer and a liquid mix. The entropy increase will be particularly large for the dissolution of a fibre-forming crystalline polymer, since crystallinity, involving a very ordered structure, corresponds to a low entropy.

The Heat Change

Since the entropy change is generally large and positive, the magnitude of the heat change is usually the deciding factor in determining whether swelling or solution occurs. From equation (i), if ΔG is to be negative, ΔH must be either negative (heat evolved, so that the mixture of polymer and liquid becomes warmer) or, if positive (heat absorbed, so that the mixture becomes cooler), low enough for its value not to exceed that of $T\Delta S$. In the mixing of a polymer and a liquid, bonds of a physical nature between polymer molecules and between liquid molecules are broken and replaced by similar bonds between polymer and liquid. Heat is absorbed in breaking bonds and heat is evolved in making them. ΔH will be the sum of the amounts of heat absorbed and evolved, so that—

$$\Delta H = \Delta H_{\text{P-P}} + \Delta H_{\text{L-L}} - \Delta H_{\text{P-L}} \qquad \text{(ii)}$$

where $\Delta H_{\text{P-P}}$ and $\Delta H_{\text{L-L}}$ are the amounts of heat absorbed in breaking polymer–polymer and liquid–liquid bonds and $\Delta H_{\text{P-L}}$ is the heat absorbed in breaking polymer–liquid bonds. The heat evolved when bonds are made will be equal in magnitude but opposite in sign to that absorbed in breaking them, so that $-\Delta H_{\text{P-L}}$ represents the heat evolved in making polymer–liquid bonds.

The amount of heat absorbed in breaking polymer–polymer and liquid–liquid bonds generally exceeds that evolved in making polymer–liquid bonds, provided that the polymer does not contain polar groups, which may form strong bonds with the liquid molecules and cause considerable evolution of heat. Theoretical treatments of heats of mixing[3] show that, if heat is absorbed in mixing—

$$\Delta H = V_{\text{M}}(\delta_{\text{L}} - \delta_{\text{P}})^2 v_{\text{L}} v_{\text{P}} \qquad \text{(iii)}$$

where V_{M} is the total volume of the mixture, v_{L} and v_{P} are the fractions of the total volume occupied by liquid and polymer respectively, and δ_{L} and δ_{P} are the *solubility parameters* of liquid and polymer. These solubility parameters, important quantities in theories of polymer–liquid miscibility, are defined by—

$$\delta = \left(\frac{L_v - RT}{V}\right)^{\frac{1}{2}} \qquad \text{(iv)}$$

where L_v is the molar latent heat of vaporisation and V the molar volume of the liquid or polymer, both at the absolute temperature T; R is the gas constant. The solubility parameter is related to attractive forces between molecules (cf. p. 503). From equation (iii) it is clear that if the positive value of ΔH is not to be greater than $T\Delta S$, then $(\delta_{\text{L}} - \delta_{\text{P}})^2$ must not be too large, i.e. δ_{L} and δ_{P} must not be very different. If $\delta_{\text{L}} = \delta_{\text{P}}$, mixing is assured by the entropy change. If, as is often assumed, ΔS does not vary much for a given polymer in a range of liquids, the value of δ_{L} determines whether swelling or dissolution occurs. For relatively non-polar polymers, liquids act as solvents if their solubility parameters lie within the approximate range $\delta_{\text{P}} \pm 1{\cdot}5$. If δ_{L} lies outside this range, the liquid will only swell the polymer, which takes up liquid until ΔH becomes equal to $T\Delta S$, so that $\Delta G = 0$.

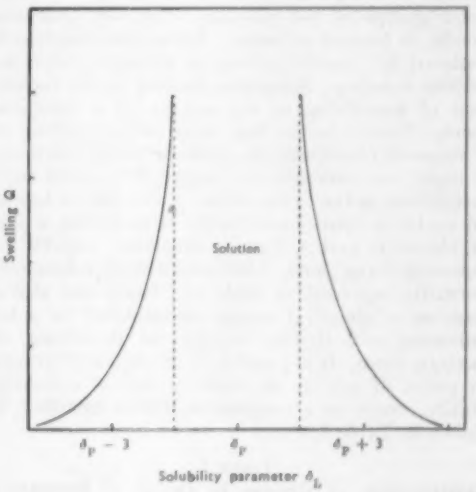


FIG. 1

The degree of swelling will be greater the closer δ_{L} is to either end of the range $\delta_{\text{P}} \pm 1{\cdot}5$. These variations of interaction with solubility parameter of a liquid are shown diagrammatically in Fig. 1, in which swelling, expressed as Q, the volume of liquid imbibed by unit volume of polymer, is plotted against δ_{L}. Between the limits $\delta_{\text{P}} \pm 1{\cdot}5$, shown by the broken vertical lines, swelling is unlimited, i.e. solution occurs.

Polar Polymers

It is important to notice that these conditions will apply only if the polymer is not too polar and strong attractive forces between the chains are absent. They will not apply if strong polymer–polymer bonds are present such as those which result from hydrogen bonds or strong dipolar forces. A number of synthetic fibre-forming polymers, such as the polyamides, possess strong interchain attraction of this kind, which often leads to a high degree of crystallinity in fibres. The heat absorbed in breaking such bonds will be large, and in the absence of compensating effects ΔH will exceed $T\Delta S$, so that solution cannot occur and swelling may be small.

Solution or increased swelling may sometimes be effected by heating, i.e. by supplying energy to

break the interchain bonds. If the solubility parameters of polymer and liquid are not too different, solution or enhanced swelling may occur. Heating will also increase the value of the entropy term in equation (i) by increasing T. Solutions formed in this way may, however, gel on cooling, or polymer may separate as polymer–polymer bonds are re-formed. A swollen polymer may exude liquid on cooling. An alternative and more useful way of effecting solution or marked swelling is to use liquids which interact strongly with the polymer, forming strong polymer–liquid bonds, so that a large amount of heat is evolved to compensate for that absorbed in breaking polymer–polymer bonds. In such circumstances ΔH may be feebly positive or even negative. Such strong interaction, in which solvent molecules are more or less firmly bound to polar groups of the polymer, often by hydrogen bonds, is termed *solvation*. Interchain bonding is replaced by equally strong or stronger polymer–solvent bonding. Solvation, leading to the formation of something of the nature of a complex, seems often to be the first stage in the swelling or solution of fibre-forming synthetic polar polymers. It may conveniently be regarded as acid–base interaction in the Lewis sense. According to Lewis, an acid is a substance capable of accepting a pair of electrons and a base a substance capable of donating them. Such definitions include substances normally regarded as acids and bases and also a number of chemical groups encountered in polar polymers and liquids capable of dissolving or swelling them. It is possible to arrange such groups in order of acidity or basicity, i.e. of solvating ability. Such an arrangement, due to Spurlin [4], is shown in Table I.

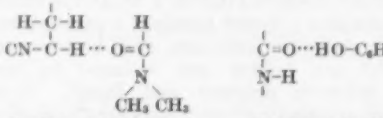
TABLE I

Classification of Groups in Order of Increasing Solvating Ability

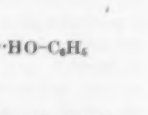
Acidic (electron-accepting)	Basic (electron-donating)
>CHCl	$-CH_2\cdot O\cdot CH_2-$
$-CHCl_2$	$-CH_2\cdot O\cdot CO\cdot CH_2-$
$>CH\cdot O\cdot NO_2$	$-CH_2\cdot CO\cdot CH_2-$
$>CH\cdot NO_2$	$>PO_4$
>CH·CN	–CO·NH–
$-C_6H_4\cdot OH$	$-CO\cdot N(CH_3)_2$
–COOH	$-C_6H_4\cdot NH_2$
$-SO_2H$	$-CH_2\cdot NH_2$

Some of the groups listed have both acidic and basic character. Thus, in esters the dominant action is basic because of the carbonyl group, which can donate electrons, but the hydrogen atoms have some acidic character. Nitrate groups have some basic character, but they are mainly acidic because of the hydrogen atoms next to the nitrate group. Groups at the top of each column are only weakly acidic or basic. Polymers containing them may possess only weak interchain forces, and may dissolve or swell in non-solvating liquids of similar solubility parameter to that of the polymer. Such weakly acidic or basic groups may, however, be solvated by a liquid containing strongly basic or acidic groups.

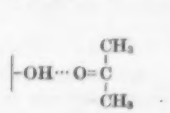
When the polymer contains strongly acidic or basic groups and strong interchain attraction exists, the ability to solvate such groups is one of the requirements of a solvent or swelling agent. A polar polymer containing acidic groups will require a liquid containing basic groups to solvate it, and *vice versa*. Thus, polyacrylonitrile, containing the acidic >CH·CN group, is solvated by basic liquids such as dimethylformamide. 6,6-Nylon and other polyamides, containing the –CO·NH– group with a basic carbonyl, require acidic liquids such as phenols. Some fibre-forming linear polymers, such as secondary cellulose acetate, contain both acidic and basic groups; the acidic hydroxy groups may be solvated by esters, ketones, pyridine, picolines, and aniline; the basic ester groups are solvated by such acidic liquids as chloroform, phenols, and acetic acid. Cellulose triacetate has only basic ester groups and requires acidic liquids for solvation. Diagrammatic representations of solvation are shown below (I–IV). All of these seem to involve hydrogen bonding between solvent and polymer, such bonding being indicated by dotted lines. Solvation of cellulose acetate and 6,6-nylon by this mechanism has been shown by infrared absorption studies [5,6], and Giles *et al.*[7] have shown, by other techniques, the possibility of such interaction between polar polymers and liquids.



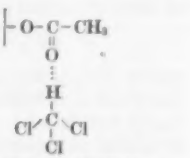
I— Polyacrylonitrile–Dimethylformamide



II— Polyamide–Phenol



III— Secondary cellulose acetate–Acetone



IV— Cellulose triacetate–Chloroform

It is, however, important to note that solvation, by itself, does not necessarily cause solution or marked swelling. The liquid must also be able to dissolve or swell the solvated polymer. Attachment of liquid molecules to the polymer will reduce their freedom of movement and thus reduce ΔS. Solvation will also render the polymer less polar in nature, acidic and basic groups neutralising each other. The solvated polymer, like a feebly polar or non-polar one, will generally mix with the solvating liquid with absorption of heat. If the heat absorbed in this mixing is so large that the overall heat change accompanying the breaking of polymer–polymer and solvent–solvent bonds, solvation, and the mixing of solvated polymer and liquid is positive and greater than $T\Delta S$, solution will not occur. Where solvation occurs, equation (ii) may be written—

$$\Delta H = \Delta H_{P-P} + \Delta H_{L-L} - \Delta H_{P-L} + \Delta H_{SP-L} \qquad (v)$$

where ΔH_{SP-L} is the heat absorbed in mixing solvated polymer and liquid. If very strong interaction between polymer and liquid occurs, ΔH_{P-L} may be large enough to ensure a negative value of ΔH or a small positive one. More generally,

however, for solution to occur, the solubility parameter of the liquid must not differ too much from that of the solvated polymer. The latter will differ from that of the unsolvated polymer and will vary somewhat with the solvating agent. It is to be expected, however, that the solubility parameters of liquids which both solvate and dissolve the polymer should lie within a certain range, which may be larger than that for solvents of a non-polar or feebly polar polymer. If the solubility parameter of the solvating liquid lies outside this range, the polymer will only swell.

We may summarise the requirements of solvents and swelling agents for fibre-forming synthetic polar polymers in the following terms. If the polymer is not too polar, solvents must have solubility parameters within the approximate range $\delta_P \pm 1{\cdot}5$. Swelling occurs if δ_L lies outside this range, being greater the closer the value of δ_L is to either end of the range. If strong interchain forces occur in a fibre-forming synthetic polar polymer, a solvent or a swelling agent must generally be capable of solvating the polymer. Unless the interaction in solvation is very strong, solution will occur only if the liquid has a solubility parameter not too far removed from that of the solvated polymer. Intermediate cases may occur where interchain forces are not very strong but the polymer contains groups capable of being solvated. In such cases non-solvating liquids may dissolve or strongly swell the polymer if their solubility parameters lie within the appropriate range. The polar groups may, however, be solvated by sufficiently acidic or basic liquids, which will dissolve or swell the polymer if their solubility parameters are not too far removed from that of the solvated polymer. In such cases there will be two ranges of solubility parameter for solvents, one corresponding to the unsolvated and one to the solvated polymer. Two ranges may occur also where the polymer possesses acidic and basic groups, each capable of solvation. In either case, the two ranges may overlap.

Determination of Solubility Parameters

A knowledge of values of solubility parameters is often important in the prediction and choice of suitable solvents and swelling agents. Since—

$$\delta = \left(\frac{L_e - RT}{V}\right)^{\frac{1}{2}} \qquad \text{(iv)}$$

the solubility parameter of a liquid, at a particular temperature T, can be obtained from its molar latent heat of vaporisation L_e and its molar volume V. The latter is simply the molecular weight divided by the density. For many liquids the value of L_e at 25°C. (in calories) can be estimated from an equation given by Hildebrand [8]—

$$L_e = 23{\cdot}7T_b + 0{\cdot}02T_b^2 - 2950 \qquad \text{(vi)}$$

where T_b is the absolute temperature of the normal boiling point of the liquid. A similar equation has been given by Walker [9], who also tabulates some values of $(L_e - RT)/V$ at 20°C. A number of methods for obtaining the solubility parameters of liquids from their physical properties have been summarised by Hildebrand and Scott [8], and values for a number of liquids given. A recent paper [10] lists solubility parameters of some liquids which dissolve or swell several fibre-forming polar polymers. Values for some typical liquids are given in Table II.

TABLE II

Solubility Parameters δ_L of Liquids at 25°C. (cal./c.c.)$^{\frac{1}{2}}$

Hexane	7·3	Dioxan	10·0
Diethyl ether	7·4	Dimethyl phthalate	10·4
*cyclo*Hexane	8·2	Pyridine	10·4
Butyl acetate	8·5	Aniline	10·8
Carbon tetrachloride	8·6	*n*-Butanol	11·4
Toluene	8·9	*m*-Cresol	11·5
Ethyl acetate	9·1	Acetonitrile	11·9
Benzene	9·2	Dimethylformamide	12·1
Chloroform	9·3	Ethanol	13·1
Methyl acetate	9·6	Propylene carbonate	13·3
Methylene chloride	9·7	Ethylene carbonate	14·7
Acetone	9·8	Ethyl carbonate	15·4

Because of the non-volatility of polymers, it is not possible to obtain their solubility parameters from latent heats of vaporisation. Small [11] has given a table of "molar attraction constants", which permit the estimation of the solubility parameter of the polymer from the molecular weight M_0 and structural formula of the repeating unit of the polymer and the density of the polymer d. A value is assigned by Small to each grouping or structure in the repeating unit. The sum of these, multiplied by the density of the polymer and divided by M_0, gives the solubility parameter of the polymer. Some of Small's constants are given in Table III.

TABLE III

Molar Attraction Constants at 25°C.

$-CH_3$	214	$>O$	(others)	70
$>CH$	28	$>CO$	(ketones)	275
$>CH_2$	133	$-CO\cdot O-$	(esters)	310
$-C\equiv C-$	222	$-CN$		410
$-C_6H_5$	735	$-Cl$		270
$-H$	80–100	6-membered ring		100

The method is illustrated below for polyvinyl chloride, the repeating unit of which is $-CH_2\cdot CHCl-$.

Molecular weight of $-CH_2\cdot CHCl-$	=	62·5
Density of polymer d	=	1·39
Molar attraction constant—		
$>CH_2$	133	
$>CH$	28	
$-Cl$	270	
Total =	431	

$$\delta = \frac{\text{Total} \times d}{M_0} = \frac{431 \times 1{\cdot}39}{62{\cdot}5} = 9{\cdot}6$$

The method works well for polymers which are not very polar but does not seem to take the influence of polar forces or hydrogen bonding sufficiently into account. In certain cases δ_P can be estimated from values for substances of low molecular weight of similar structure to that of the polymer. Thus Walker [9], from values for acrylonitrile, propionitrile, and adiponitrile, estimates the solubility parameter of polyacrylonitrile to be 15·4.

Other methods of determining the solubility parameters of polymers use liquids of varying δ to determine the range within which solution occurs. The value of δ_P may be taken as the mid-point of this range, although this is only an approximation [13]. Alternatively, the polymer may be cross-linked so that it can only swell. Swelling will be greatest in the liquid whose solubility parameter is closest to that of the polymer. A graph of swelling against δ_L will show a maximum, the δ_L value corresponding to this being taken as the solubility parameter of the polymer. These methods may be rather insensitive if solvation causes the solubility parameter of the solvated polymer to vary with the liquid. Some values of δ_P, which should be regarded as approximate and likely to vary if solvation occurs, are given in Table IV.

TABLE IV

Solubility Parameters δ_P of Polymers (cal./c.c.)$^{\frac{1}{2}}$

Polyvinyl acetate	9·1–9·4
Polyvinyl chloride	9·5–9·9
Vinyl acetate–vinyl chloride copolymer	10·4
Vinyl acetate–acrylonitrile copolymer	10·5
Polymethacrylonitrile	10·7
Polyethylene glycol terephthalate	10·7
Secondary cellulose acetate	11·0
Polyvinylidene chloride	12·2
6,6-Nylon	13·6
Polyacrylonitrile	15·4

Some of these values are high. As shown in Table II, most common organic liquids have relatively low solubility parameters. It may therefore be difficult to find readily available solvents or swelling agents for a polymer with a high δ_P. The solubility parameter of the polymer may be reduced by the introduction of other groups, such as methyl, if this does not lead to undesirable properties. Table IV shows that the solubility parameter of polymethacrylonitrile is considerably lower than that of polyacrylonitrile. Copolymerisation also may reduce δ_P. The solubility parameters of the copolymers of acrylonitrile with vinyl acetate or vinyl chloride, met in dynel and Vinyon N (Carbide & Carbon Chemicals Co.), are considerably lower than that of polyacrylonitrile. Copolymerisation does not, however, always reduce δ_P, and the solubility parameter of the vinyl acetate–vinyl chloride copolymer is greater than that of polyvinyl acetate or polyvinyl chloride.

Liquid Mixtures

An interesting consequence of the relationship between the solubility parameter of a liquid and its swelling or solvent action for polymers is that two liquids, either one of which, by itself, will swell a polymer to only a limited extent, may together form a mixture which has considerable swelling power or even dissolves the polymer. The solubility parameter δ_M of a mixture of two liquids may be expressed—

$$\delta_M = \delta_1 v_1 + \delta_2 v_2 \qquad \text{(vii)}$$

where v_1 and v_2 are the volume fractions of the two liquids in the mixture. If δ_1 and δ_2 lie on different sides of δ_P, δ_M may be closer to δ_P than δ_1 or δ_2, and enhanced swelling or solvent action may occur. For example, secondary cellulose acetate is not dissolved by ethyl acetate (δ = 9·1), which solvates and swells it. Addition of a little ethanol (δ = 13·1), also a non-solvent, causes solution, because δ_M falls within the appropriate range of solubility parameters. Similarly, the copolymer of vinyl acetate and vinyl chloride is not dissolved by either diethyl ether (δ = 7·4) or acetonitrile (δ = 11·9) alone, but a mixture of these liquids acts as a solvent.

Temperature Dependence

The solubility parameters of liquids vary very little with temperature, the average decrease for a rise of one degree Centigrade being only 0·015 unit. No information is available on the change of δ_P with temperature, but it is reasonable to assume that it is similar to that of liquids, particularly if the polymer is not very crystalline. Since we are concerned with conditions under which liquid and polymer are at the same temperature, the net effect on solvent or swelling action of variations in solubility parameter should be small. The $T\Delta S$ factor in the free-energy equation is usually of greater importance in determining variations of polymer–liquid interaction. Desolvation may occur at high temperatures, however, if the bonds between polar groups of liquid and polymer are not very strong.

APPLICATIONS

The principles outlined above may now be applied to the interaction of some specific fibre-forming synthetic polar polymers and liquids.

POLYVINYL ACETATE (solubility parameter 9·1–9·4) is an example of a polymer which is not very polar but contains groups capable of being solvated. The repeating unit, $-CH_2{\cdot}CH(O{\cdot}CO{\cdot}CH_3)-$, possesses a weakly basic carbonyl group, which may be solvated by acidic liquids. The weakly polar nature of this polymer makes it soluble in non-solvating liquids which have solubility parameters between about 8·3 and 10·4, such as benzene, toluene, and the lower esters and ketones. Acidic liquids such as chloroform and tetrachloroethane are good solvents because of solvation, which may also be responsible for the fact that methanol, with a high solubility parameter, is a solvent, though a poor one, for some samples of the polymer.

POLYVINYL CHLORIDE has a solubility parameter between 9·5 and 9·9. The acidic hydrogen in the repeating unit $-CH_2{\cdot}CHCl-$ may be solvated by ketones and esters, and those with δ values between about 8·5 and 11·0 may act as solvents. Increasing the amount of chlorine, as in the fibre PeCe (Agfa), does not seem to alter the solubility parameter much but perhaps tends to render the polymer more basic, so that chlorinated hydrocarbons with solubility parameters between 9 and 10 are good solvents.

VINYL ACETATE–VINYL CHLORIDE COPOLYMERS have a solubility parameter of about 10·4. Basic acetate groups and acidic hydrogen atoms in the $-CH_2{\cdot}CHCl-$ units make it capable of solvation

and solution by acidic liquids such as chlorinated hydrocarbons and nitroparaffins with solubility parameters between 9 and 12·6, and by basic liquids such as the lower ketones and esters with δ values greater than about 9.

POLYVINYLIDENE CHLORIDE (SARAN), with the repeating unit $-CH_2{\cdot}CCl_2-$, has strong interchain bonds and a solubility parameter of about 12·2. Heat may be necessary to effect solution, and this polymer may be solvated and dissolved by basic solvents of appropriate δ such as dioxan (δ = 10) and *cyclo*hexanone (δ = 9·9), which may solvate acidic hydrogen atoms, and by acidic solvents such as chloroform and tetrachloroethane, which may solvate basic chlorine atoms.

CELLULOSE ACETATE, in the form of the secondary acetate, is another example of a fibre-forming polymer possessing both acidic and basic groups. It is soluble in acidic liquids with sufficiently high solubility parameters (ca. 12), such as the cresols and nitromethane. Acidic liquids with lower values of δ, such as chlorinated hydrocarbons and the higher nitroparaffins, solvate and swell the polymer but do not dissolve it. This polymer is, however, dissolved by basic liquids, such as methyl acetate, acetone, dioxan, and pyridine, with solubility parameters between 9·5 and 12. These presumably solvate hydroxyl groups, and the polymer with acetyl groups solvated seems to have a higher solubility parameter than that with hydroxyls solvated. The fully acetylated triacetate, without hydroxyl groups, is soluble only in acidic liquids, although the range of solubility parameters is fairly wide, from chloroform (δ = 9·3) to *m*-cresol (δ = 12·6). It is not soluble in basic liquids within this range, although they may have some swelling action.

POLYACRYLONITRILE, known in fibre form as e.g. Orlon (DuP) and Acrilan (Chemstrand), has a very high solubility parameter (15·4). This means that commonly available liquids such as the simpler esters and ketones will not dissolve or swell it appreciably. Liquids of high solubility parameter are required, and solvation also seems to be important. Although the polymer is soluble, at relatively high temperatures, in liquids which have high δ values but which are unlikely to solvate the acidic hydrogen of the $-CH_2{\cdot}CN-$ repeating unit, separation of polymer or gel formation generally occurs on cooling. For solution at room temperature, solvation by basic liquids of high solubility parameters seems to be necessary. This is shown in Table V by some results from a paper by Walker [9].

TABLE V

Solvent Action for Polyacrylonitrile

Liquid	δ (cal./c.c.)$^{\frac{1}{2}}$	Solubility
Ethyl carbonate	15·4	Soluble at 50°c.
Malononitrile	15·1	Soluble at 100°c.
Succinonitrile	14·9	Soluble at 100°c.
Glutaronitrile	14·3	Soluble at 105°c.
α-Piperidine	13·6	Soluble at 105°c.
Propiolactone	13·4	Soluble at 110°c.
γ-Pyrone	13·3	Soluble at 150°c.
Adiponitrile	13·2	Soluble at 175°c.
Butylene carbonate	12·1	Soluble at 185°c.
Dimethyl sulphone	14·6	Soluble above 100°c.
Ethyl methyl sulphone	13·4	
Diethyl sulphone	12·5	
Methyl propyl sulphone	12·5	
Dipropyl sulphone	12·0	Non-solvent
N-Formylmorpholine	12·5	Solvents at room temperature
Dimethylformamide	12·1	
N-Acetylpyrrolidine	12·5	
N-Acetylmorpholine	11·6	
Diethylformamide	10·6	Non-solvents
Diethylacetamide	9·9	

POLYAMIDES, such as 6,6-nylon, also have high solubility parameters. Interchain attraction, due to hydrogen bonding, is strong, and solvation by liquids capable of forming hydrogen or other dipolar bonds with the polymer seems to be a requirement for solution or marked swelling. Solvents for polyamides include acids such as formic (δ = ca. 14) and phenols with solubility parameters around 13. These are believed to form hydrogen bonds with the basic oxygen of the $-CO{\cdot}NH-$ link. Valentine [12] has studied the swelling of cross-linked 6,6-nylon in about twenty phenols and found solvent action to be correlated with their ability to form hydrogen bonds. Internal hydrogen bonding, as in guaiacol, *o*-chlorophenol, and *o*-nitrophenol, reduced swelling considerably. It is of interest to note that hydrogen-bond-breaking substances such as lithium and calcium chlorides in methanol are solvents, and so are Lewis acids such as antimony and arsenic trichlorides, which are also believed to solvate basic oxygen atoms. Recently, Ford and Marshall [6] have found that titanium chloride–methanol and stannic chloride–methanol complexes have good solvent properties for 6,6-nylon and have shown by infra-red absorption spectroscopy that complex formation occurs and involves the basic oxygen atoms of the polymer. Aqueous chloral hydrate (70%) has been found to be a good solvent for polyamides.

POLYETHYLENE GLYCOL TEREPHTHALATE, with a solubility parameter of about 11, exhibits strong interchain attraction, which seems to be a consequence of close packing rather than strong dipolar attraction. If this attraction is overcome, e.g. by heating, the polymer is soluble in liquids with solubility parameters not too far removed from 11. Thus, the lower esters and ketones, nitrobenzene (δ = 10), benzyl alcohol (δ = 11), and dioxan (δ = 10) are solvents. Solvation also may occur, since the polymer is soluble in phenols and in phenol–tetrachloroethane mixtures, and Giles [7] has suggested that the ester groups of the polymer may act as proton donors.

CONCLUSION

It should be noted that the use of solubility parameters and the concept of solvation as guides to the swelling or solvent properties of organic liquids for synthetic polar polymers is approximate. Since—

$$\Delta G = \Delta H - T\Delta S \qquad (i)$$

then, in addition to differences in ΔH, variations in ΔS, which may arise in cases of solvation of the same polymer by different liquids, will affect the value of ΔG and therefore swelling or solvent power. An increase of temperature may cause desolvation, if polymer–solvent bonds are not too strong, and thereby modify polymer–liquid interaction. It is, of course, essential that the liquid molecules should not be too large, so that they can penetrate between polymer chains. In spite of these additional factors, the concepts of solubility parameter and solvation generally provide at least a good working guide to the interpretation of the interaction of polar synthetic polymers and organic liquids.

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CORRESPONDENCE

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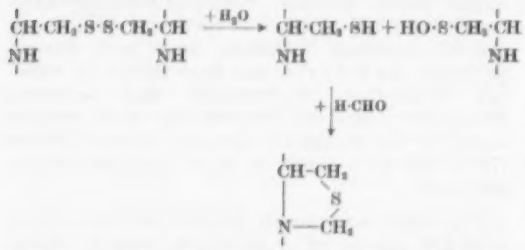
The Reaction of the Cystine of Wool with Formaldehyde

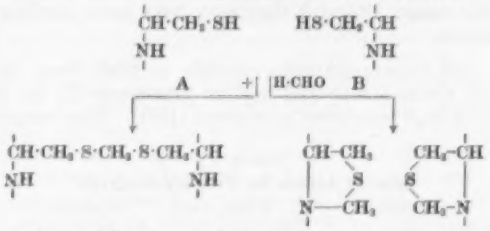
The reaction between wool cystine and formaldehyde has been studied in some detail [1, 2]. No reaction between them occurs at room temperature, but at 70°C. a maximum of about one-third of the cystine will react. It was suggested that combined thiazolidine-4-carboxylic acid was formed from one sulphur atom of the cystine by the following reactions—



Evidence for the presence of thiazolidine-4-carboxylic acid was obtained from the fact that during the determination of cystine, when the hydrolysate was treated with sodium bisulphite followed by phosphotungstic acid, the colour of the solution showed a gradual intensification over a considerable period of time in a similar manner to synthetic thiazolidine-4-carboxylic acid. The fate of the sulphenic acid group derived from the second sulphur atom of the cystine remained uncertain: it may remain free or condense with an adjacent amino group of the peptide chain [2].

These reactions with formaldehyde took place in acid or neutral solution; in alkaline solution at elevated temperatures lanthionine was formed from some of the cystine simultaneously with thiazolidine-4-carboxylic acid.

A distinction between the reactions of Subfractions A and B of the wool cystine [3] was made. In neutral or acid solution Subfraction B reacts to give thiazolidine-4-carboxylic acid and Subfraction A does not react; in alkaline solution Subfraction B gives thiazolidine-4-carboxylic acid, and Subfraction A gives lanthionine. When wool was reduced with thioglycollic acid and then treated with formaldehyde, it was concluded that Subfraction B gave thiazolidine-4-carboxylic acid, and Subfraction A gave djenkolic acid, the presence of these amino acids in the respective hydrolysates being demonstrated by paper chromatography—



The validity of these conclusions, however, depends on the assumption that both thiazolidine-4-carboxylic acid and djenkolic acid are stable to acid hydrolysis. Information on the stability of the two acids towards hydrochloric acid is limited. Ratner and Clarke [4] found that, when thiazolidine-4-carboxylic acid was distilled at constant volume in N. hydrochloric acid, formaldehyde and cysteine were produced. Lillevik and Sandstrom [5] also found that thiazolidine-4-carboxylic acid yielded formaldehyde when hydrolysed with hydrochloric acid, and Middlebrook and Phillips [2] found that the acid dissociated to the extent of 3·6% into cystine and formaldehyde during 4 hr. refluxing with 5N. hydrochloric acid. Van Veen and Hyman [6] stated that no cleavage of djenkolic acid occurred on boiling with different concentrations of hydrochloric acid, but Lillevik and Sandstrom [5] found that it was split to the extent of 85% in boiling 20% hydrochloric acid for 24 hr.

In view of the limited amount of information about the products of reaction, a further investigation was made. Djenkolic acid and thiazolidine-4-carboxylic acid were synthesised as described by Armstrong and du Vigneaud [7] and Ratner and Clarke [4] respectively. They were shown to be free from other amino-acid contaminants by paper chromatography.

Djenkolic acid (10 mg.) was boiled under reflux for 24 hr. with 20 ml. of 5N. hydrochloric acid, the hydrogen chloride removed by repeated distillation *in vacuo* with the addition of water, and the residue dissolved in water and examined on a one-dimensional collidine chromatogram [8]. Besides the spot due to unchanged djenkolic acid, a strong yellow spot due to thiazolidine-4-carboxylic acid was also present. When thiazolidine-4-carboxylic acid (10 mg.) was similarly treated, a spot due to djenkolic acid was observed in addition to that due to unchanged thiazolidine-4-carboxylic acid.

These experiments establish that, on boiling with hydrochloric acid, djenkolic acid is partly converted into thiazolidine-4-carboxylic acid and thiazolidine-4-carboxylic acid is partly converted into djenkolic acid. It seems probable that under the hot acid conditions partial splitting of the CH_2–S bonds in these compounds occurs with the addition of water. Recombination may then take place to give either thiazolidine-4-carboxylic acid or djenkolic acid. The proportions of each compound present in the final mixture will depend on the precise experimental conditions used and the relative stabilities of the two compounds. Under these conditions it is obviously very difficult to decide whether djenkolic acid or thiazolidine-4-carboxylic acid residues were originally present in a formaldehyde-treated protein that has been hydrolysed with acid and examined chromatographically, and the final compounds present in the hydrolysate may bear little actual relation in nature and amount to the residues present before hydrolysis.

It may well be the case that only one of the compounds, thiazolidine-4-carboxylic acid or djenkolic acid, is formed in all instances when reduced wool reacts with formaldehyde, and not either, depending on the conditions.

In alkaline solution, formaldehyde reacts with normal wool to give thiazolidine-4-carboxylic acid (or djenkolic acid) and under more drastic conditions lanthionine. In this case we have two competing reactions— reaction of the cystine with formaldehyde to give thiazolidine-4-carboxylic acid and reaction with the alkali in the solution to give lanthionine. The final amounts of these two end-products will depend on the relative rates at which the two reactions take place.

These results, together with those on the reaction of wool with alkali reported recently [9], require that some revision be made of the earlier views. In general, it may be said that there is no definite evidence for any rigid distinction between two fractions, A + B and C + D, or between Subfractions A and B, of the cystine of wool on the basis that they form different end-products when treated with a particular reagent. The suggestion that small ring-structures containing cystine, such as are present in oxytocin, vasopressin, and insulin, may be present in wool [10] receives much less support, though it is not ruled out by the present evidence.

The evidence that the different cystine residues vary in ease of reaction among themselves, however, remains largely unaffected. The differences in reactivity are dependent on the nature of the reagent and any previous chemical treatment the wool has undergone [11, 10]. The cause of this difference in reactivity is, however, not yet fully elucidated. Differences in the polar character of the groups adjacent to the cystine residues [11] or differences in accessibility of the cystine of the fibre towards the reagent [12] may be the determining factor, but a final decision does not seem possible at present.

S. Blackburn

Wool Industries Research Association
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Leeds 6

10th July 1957

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Scouring of Blended Worsteds containing Polyester Fibre

During the past two years increasing quantities of polyester fibre have been blended with wool in the manufacture of worsted suitings. For these cloths finishers have used scouring routines which they have found by experience to be adequate for processing similar cloths made wholly of wool. It has become increasingly apparent, however, that finishers are experiencing difficulty in achieving with the blended cloths the standard of cleanliness which they have hitherto obtained with all-wool worsteds, despite the fact that the amount of fatty matter present in the former in the loom state (usually ca. 3%) is appreciably lower than the amount normally present in all-wool worsteds (usually 4–5%).

Tests made on a number of samples taken from commercially scoured pieces showed that the residual fatty matter (determined by extraction with diethyl ether) was rarely less than 0·5%, but more frequently it was within the range 0·6–1·2%, with occasional results approaching 2%. In comparison, no difficulty is experienced in scouring all-wool worsteds to a residual fatty content of

0·3% or less, and values of 0·15% or lower are frequently met in commercially scoured pieces.

A residual fatty content in a finished worsted cloth approaching or over 1·0% is undesirable, because it may lead subsequently to a number of objectionable features, all of which have been encountered frequently in these blended cloths and in garments made from them, viz. inferior fastness to rubbing, staining of labels, staining of pockets, linings, and bindings, particularly where maintained in intimate contact with the cloth at sewings, a liability to retain unevenly dust, e.g. flour, face powder, during wear. Defects involving staining are particularly pronounced, because the fatty matter is frequently highly coloured as the result of the association with it of significant amounts of disperse dyes used for dyeing the polyester fibre. These dyes are soluble in oil to a much greater extent than are the dyes used for dyeing wool.

Although in industrial processing the combing oil is applied principally to the wool component, it seems likely that it will redistribute itself subsequently to blending, so that by the time the piece-scouring stage is reached it is probably fairly evenly distributed between the two fibres. The difficulty of removing combing oils from polyester fibre has been clearly demonstrated in the laboratory. Combing oils (nominally 3·5%) were applied at the gill-box to undyed tops of each fibre. Blends (55 parts polyester fibre : 45 parts wool) were also prepared using wool oiled with 7·0% combing oil and polyester fibre to which no addition of combing oil was made. Five samples of each top, each weighing 10 g., were scoured successively in a solution containing 0·1% soap (Flanola) and 0·5% soda ash. After scouring, the first, third, and fifth samples were rinsed off, dried, and used for the determination of residual fatty matter by extraction with diethyl ether.

Combing Oil	Fibre	Fatty Matter (%) Before Scouring	After Scouring
Topsol*	Polyester	3·6	2·3
	Wool	3·4	0·2
	Wool–polyester blend	3·7	2·0
Control combing oil	Polyester	4·0	1·7
	Wool	3·3	0·2
	Wool–polyester blend	3·7	1·3

* Topsol was known formerly as "Class A (1949) Combing Oil".

The results in the table show that, whilst the two combing oils are readily removed from wool under the scouring conditions used, they are much less readily removed from polyester fibre, either alone or blended with wool, even though in the latter case the oils have been applied to the wool component only. There is also some suggestion that Control Combing Oil is more readily removed from polyester fibre than is Topsol*.

The phenomenon has also been demonstrated by microscopic observations of oiled fibres mounted in detergent solution (soap and soda ash). With oiled wool fibres, the well known preliminary stage of "rolling-up" of the oil into spherical droplets, prior to their removal from the fibre, was complete in a few seconds. With polyester fibre, movement of the oil on the fibre surface tended to cease when the droplets had reached a hemispherical shape on the fibre surface, there being little detachment of the oil drops from the fibre. A number of other natural and man-made fibres were examined in this way, but only polyethylene was found to behave like polyester fibre, all other fibres examined behaving like wool. This problem is being further examined.

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R. S. Hartley

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2nd September 1957

Brooke, Simpson & Spiller

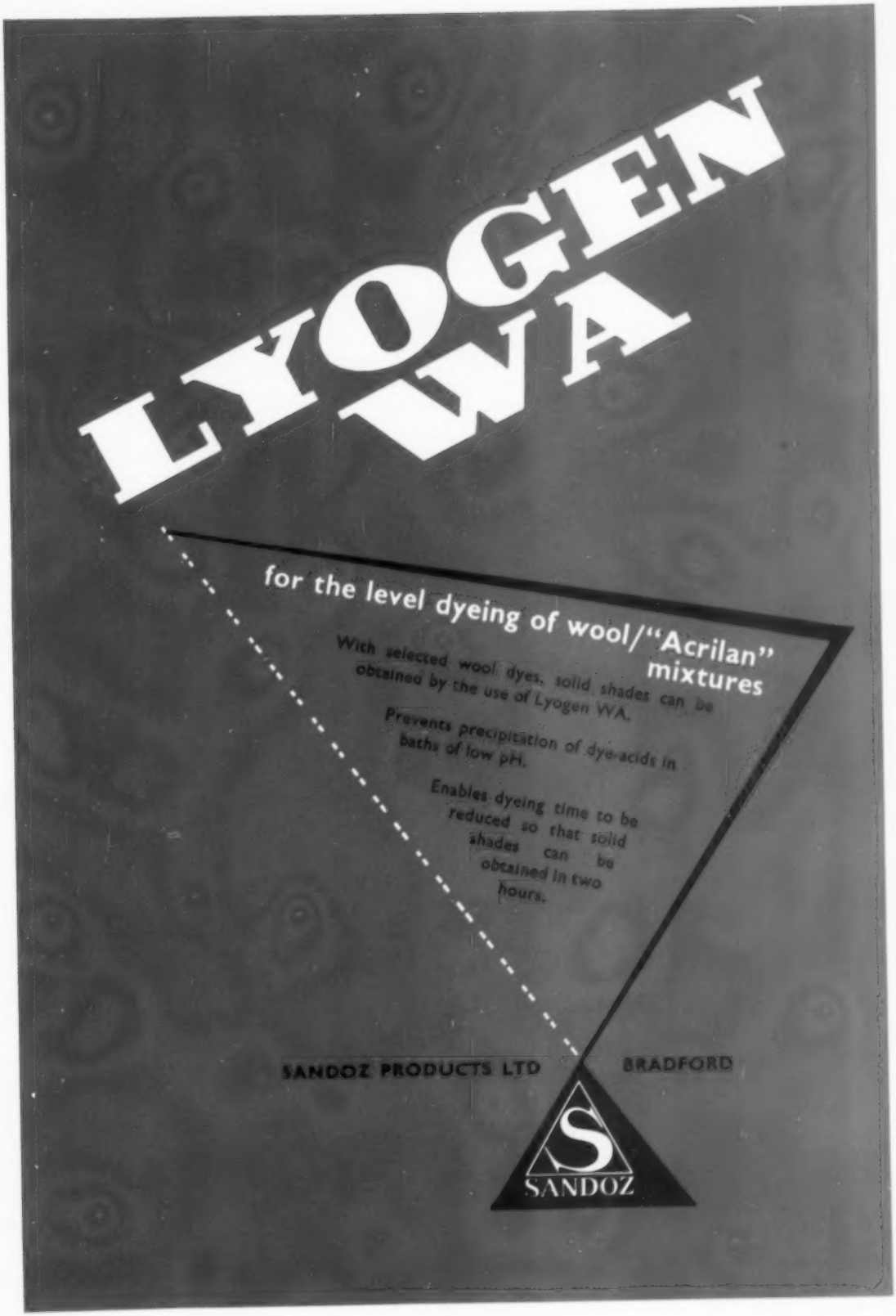
W. H. Cliffe, in his researches into the history of W. H. Perkin's discovery of Mauve, and that of the factory at Greenford Green [1], has brought to light many hitherto unknown facts regarding the transfer of these works to Messrs. Brooke, Simpson & Spiller. The present writer is now probably the last survivor of those who had personal connections with this firm. The following notes about the firm may be of interest to members of the Society.

I joined the firm at the invitation of Professor A. G. Green in 1903, taking charge of the dye-standardising and technical service work, and remaining there until 1905. At this time the staff consisted of the Commercial Manager, the Secretary, five chemists, one dyer, the Chief Engineer, and the Manager of the Printing Ink Department, with Professor A. G. Green acting as Consultant Chemist. Of the chemists, W. S. Simpson and W.(?) Evershed had a lifetime connection with the firm. When it went into liquidation in 1905 W. S. Simpson went into business under his own name. Evershed had joined the neighbouring firm of Clark, Nichol & Coombe ("Clarnico"), chocolate and sweet manufacturers.

At the time I joined the firm, an effort was being made to put the business upon a more satisfactory footing and to restore something of its former glory. The late Dr. H. Levinstein and others have placed on record the difficulties under which the British dye industry laboured at the period. These conditions and the lack of financial backing prevented these efforts from being successful.

The accompanying price-list of Brooke, Simpson & Spiller's gives an idea of the range of dyes and types of alizarin being offered for sale as early as 1876.

The price-list contains illustrations of the Greenford Green Works, already shown adequately in the *Journal* [2], and of the Atlas Works at Hackney Wick, reproduced here. The latter is reasonably truthful, except that the Dyeing Laboratory and the Magenta shed should be in line with each other and not one in front of the other as shown. A brief description of the works follows. For ease of reference, letters and numbers have been added to the margin of the illustration.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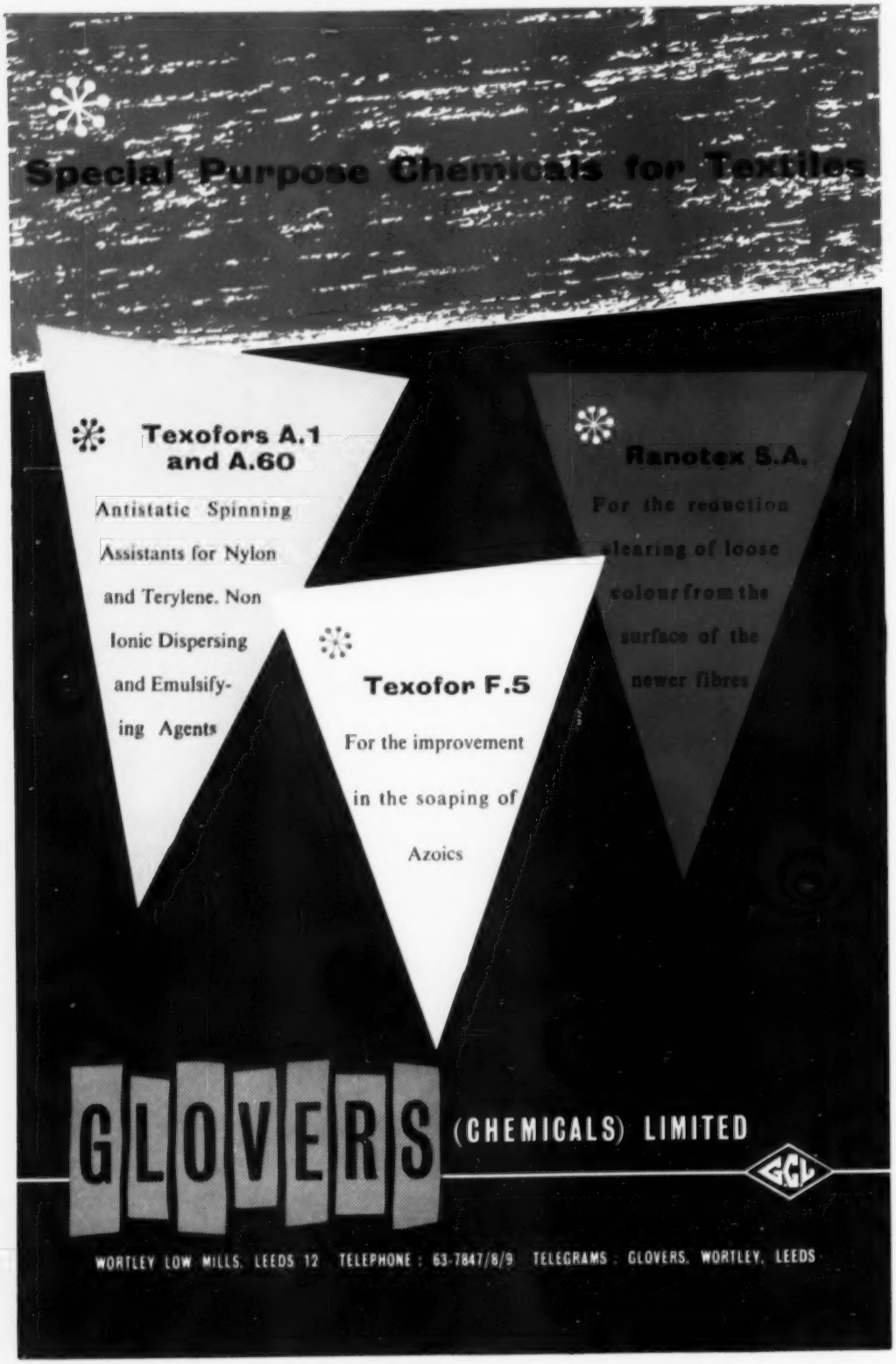
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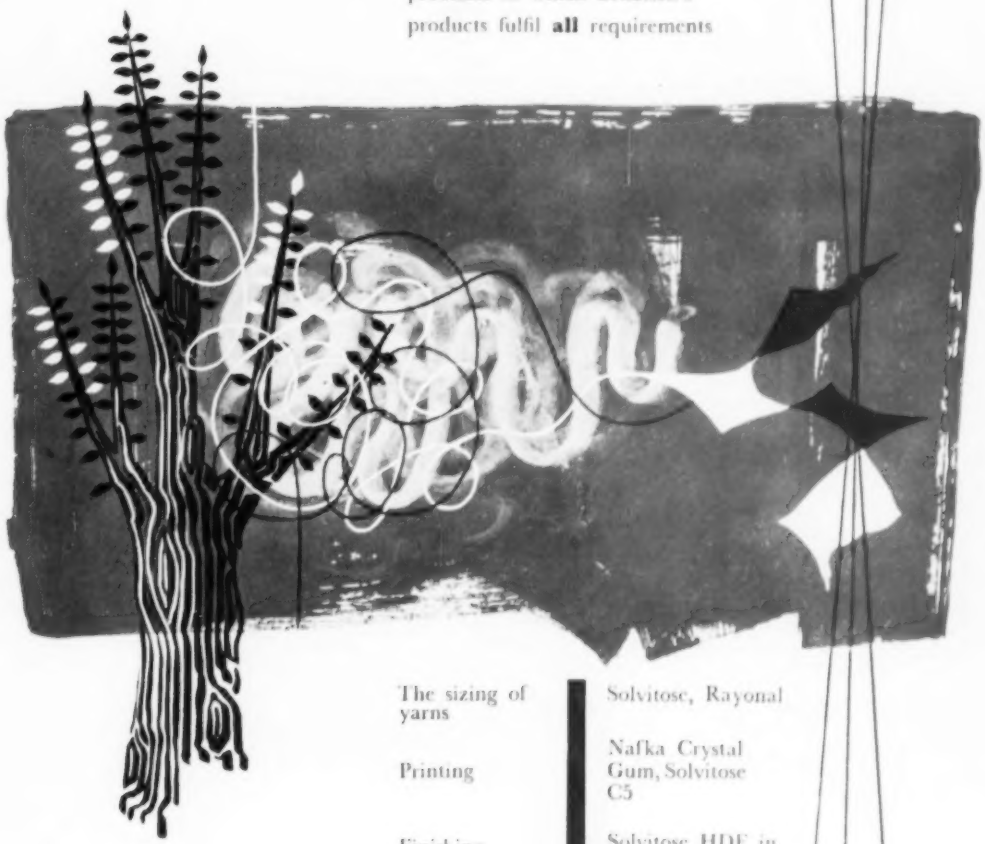

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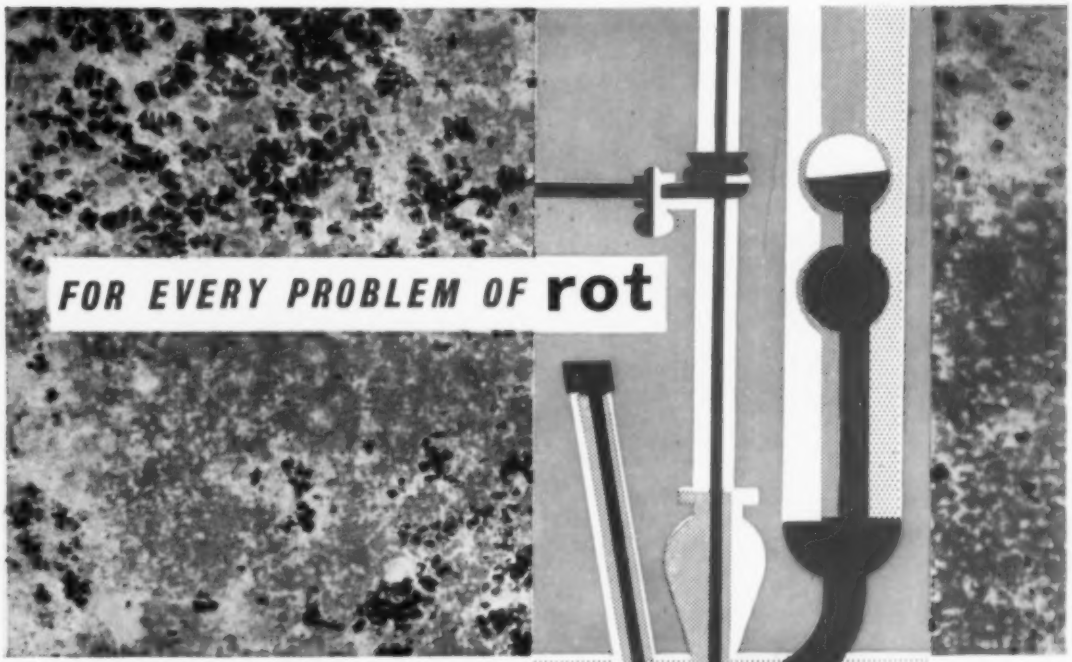

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Inns and the Textile Trade

No. 11. *'The Fleece,' Bretforton, near Evesham.*

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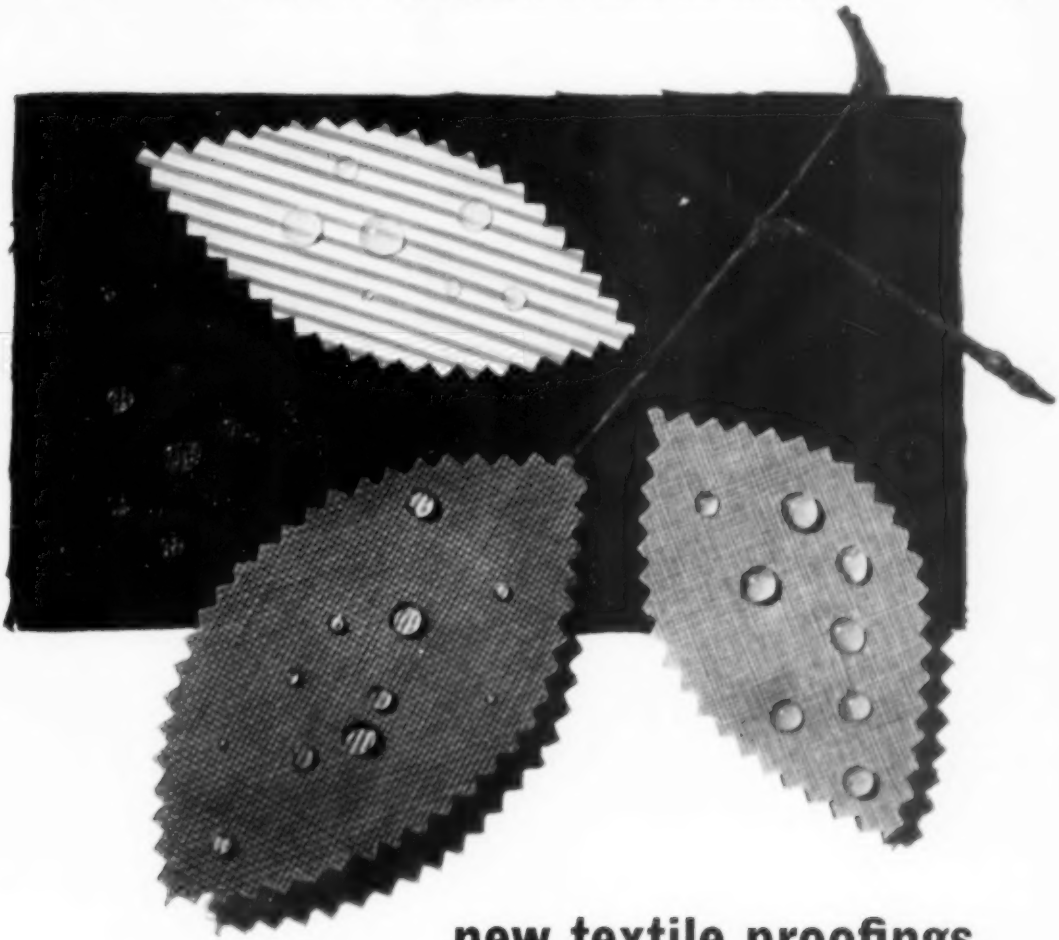

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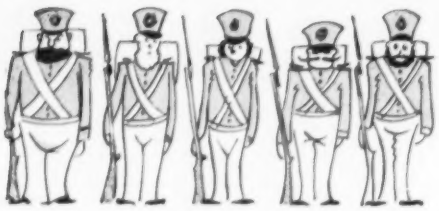

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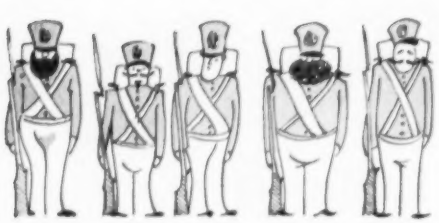

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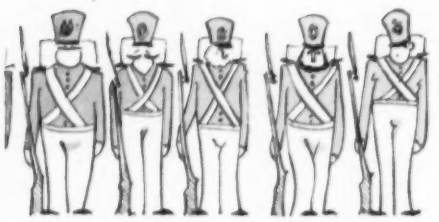

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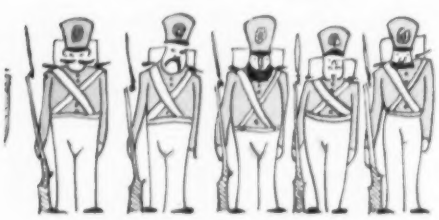

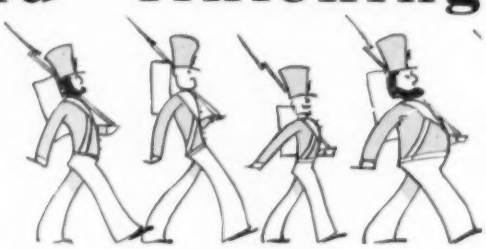

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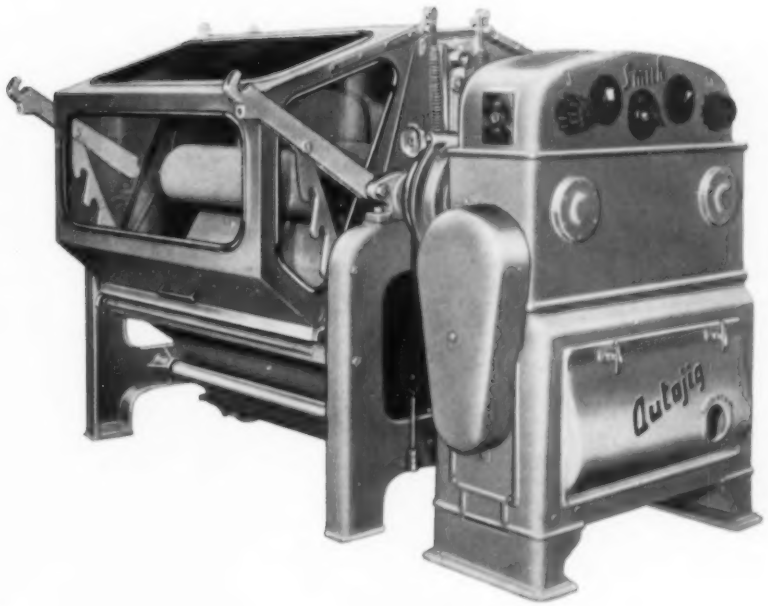

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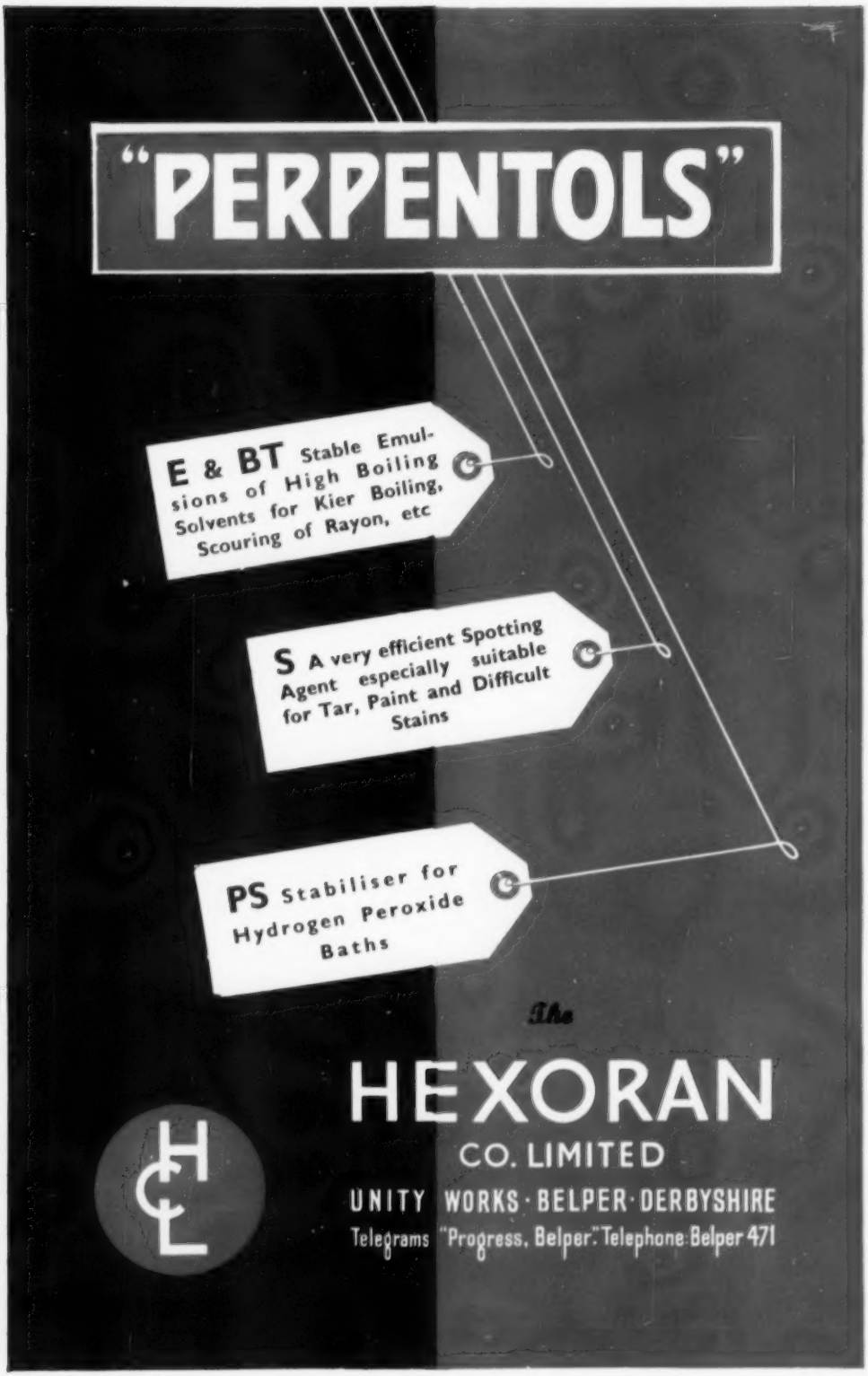
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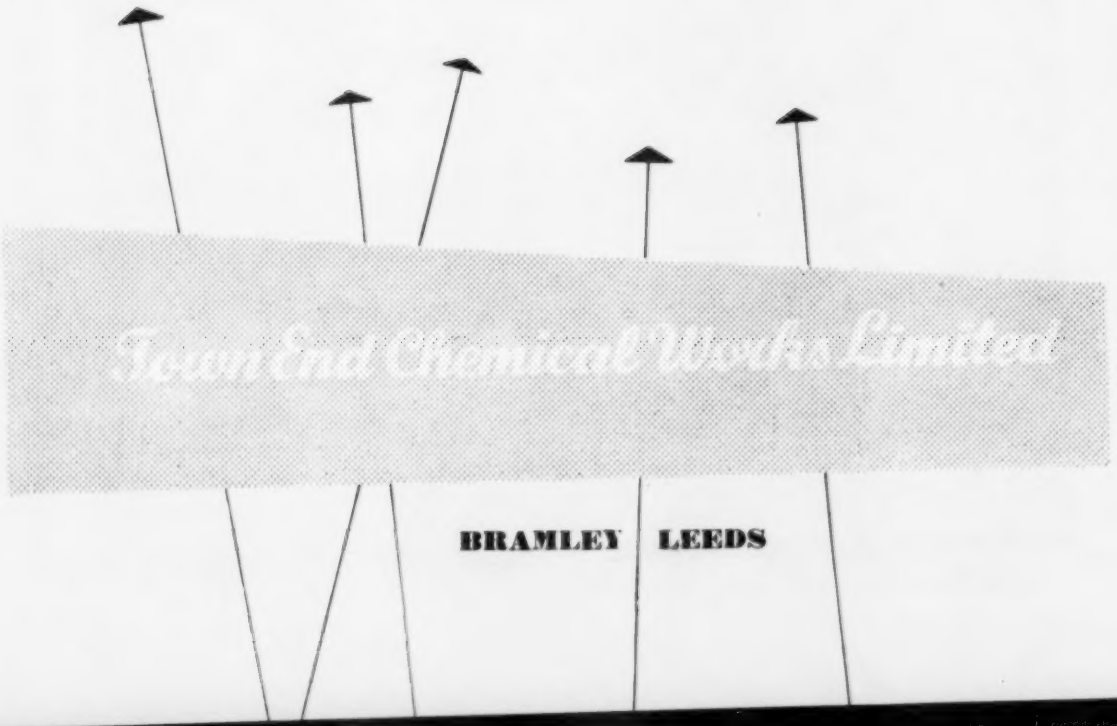

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B.B.	
B.	
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Do. do. X.	
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Do. R.	
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ANILINE SALT, FOR PRINTING BLACK.	
GREENS.	
Green Crystals, Blue Shade ...	
Do. do. Yellow do. ...	
Atlas Green	

Brooke, Simpson & Spiller's Aniline Dye Factory at Hackney Wick (ca. 1876)

M 2 is the office block, the office staff being on the upper floor and the rear of the ground floor. To the right of the door is the gatehouse and kitchen, while on the left is a staff cloakroom and dining room. As the works were situated in the East End of London, there was no suitable restaurant in the area, so some provision for staff meals had to be made.

The three-storey building (K 2) with the figure of Atlas over the centre was the finished-product warehouse and packaging department. The long building (G–H 2–3) to the left of the warehouse contained the engineering workshops and the stables. The larger building (F 2) accommodated the nitrobenzene and other intermediates plants. At a later date the site centred on B 3 was occupied by plant for the manufacture of sulphuric acid, nitric acid, various dyes, and chemical stores. The buildings on the extreme right with three ventilators and seven skylights (L–M 3–5) were devoted to the printing-ink department. K 3 was built originally for manufacturing purposes but was later converted into the dyehouse. The chemical laboratory, a one-storey building (F 4), partly hidden by the chimney, was an interesting example of an early works laboratory containing, in an elementary form, a number of features found in a modern works laboratory (apparatus store, library, balance room, laboratories, and a small-scale plant room). The most interesting item in the small-scale plant room was the plant built by Green for his experiments on the manufacture of Primuline. The large building with the clock-tower (J 5) was the Roseine (Magenta) plant. No Magenta was being manufactured in 1903, and the building was falling into disrepair. It still contained a number of large tanks, about 4 ft. deep, built up from metal plates and braced by tie-rods. These tanks were formerly used for crystallising Magenta. During the Franco-Prussian war, when the products of the French makers were no longer available, the firm enjoyed a monopoly of this dye and its derivatives. For quite a period Magenta was "big money" for the firm.

The buildings along the canal side were used for the manufacture of Induline and Sloeline (Nigrosine), the Rosaniline Blue series, azo dyes, and pigments.

The dyes listed in the 1876 price-list include several shades of Alizarin, Roseine (Magenta), crystal and cake, Ponceau, Nicholson's Blue (Alkali Blue) 6B to B and R shades, Nicholson's or Alkali Violet, Spiller and Regina Purples, Phosphine, Aniline Orange, Primrose, Bismarck Brown, Imperial or Spirit Blues, Silver Grey (Induline), Basic Greens, and Aniline Oil for printing (Aniline Black).

During my time at Hackney Wick the firm had a useful trade in sulphuric acid, nitric acid, aniline,

ALIZARINE.

SCARLET SHADE FOR PRINTING.

RED SHADE FOR DYEING.

BLUE SHADE FOR DYEING AND PRINTING.

PURPLE SHADE FOR PRINTING.

and several of its derivatives. The firm could not compete with the German firms for the larger contracts but had some faithful customers for sundry uses, e.g. Sloeline for boot polishes, Phosphine and the Bismarck Browns for the leather stainers. Good quantities of pigments were manufactured including those from organic dyes and mineral pigments such as the chrome yellows and oranges and Prussian blue. A large proportion of these pigments was absorbed by the printing-ink department, and this, in turn, found an outlet for its products amongst the London printers. To a relatively inexperienced young man these contacts with the many sundry colour-using trades in the London area gave interesting and useful experience. Maybe I faced its problems the better because of some earlier experience as a "Voluntär" in the laboratories of the Badische Anilin- und Soda-Fabrik at Ludwigshafen.

At this time there was an interesting trade in dyes for the Far East for sale in the bazaars to the native village dyers. These men were familiar with the use of natural dyestuffs requiring large amounts of dyeing agent. The packages of aniline dyes, mostly in small containers, consisted of highly diluted products suitable for their primitive methods and by no means unprofitable to the dye manufacturers. It was a trade which called for careful supervision. The tins had to be full, as an empty space suggested that the contents had been tampered with. Glossy pictorial labels in several colours and covering the whole of one side of the tin as well as a glossy wrapper approximating to the colour of the dye within were of major importance. For some markets the design must not contain any suggestion of an animal or a human figure, while in others such figures were a good sales feature. I can recall one such series in which the cost of the tin and the wrappers exceeded that of the contents. Imitation Magenta crystals consisted of a tinted starch–gum base given the characteristic green lustre by spraying with a solution of Magenta.

Professor Meldola had connections with the firm but left it in 1885 [3]. It is not generally known that Mr. Ernest Hickson, one the founder members of the Society and President from 1925 to 1927, was associated with Brooke, Simpson & Spiller, first in the laboratory and later on the commercial side. He was their sales representative in Bradford from 1884 in order to develop the sale of the new synthetic dyes in Lancashire and Yorkshire, where previously little other than natural dyes had been used. About 1890 he was a director of the company, but he left in 1893 and started in business under his own name. He had formed the opinion that the Company was falling behind the Germans in research and development, and that the partners were taking too large profits out of the business, thus weakening the business, an opinion which was common amongst those I worked with at Hackney Wick. Mr. Hickson had a high opinion of the integrity and ability of Edward Brooke and maintained a close personal friendship with W. S. Simpson during the latter's lifetime (private communication from Mr. Bernard Hickson, Mr. Ernest's son).

H. Wilkinson

44 Fulwood Hall Lane
Fulwood
near Preston
Lancashire

3rd September 1957

[1] Cliffe, W. H., *J.S.D.C.*, **73**, 312 (1957).
[2] Rowe, F. M., *ibid.*, **54**, 556 (1938).
[3] *Ibid.*, **31**, 260 (1915).

The Adsorption of Dyes by Cellulose Acetates

Recent experiments here upon the action of dyes upon monolayers of acetates and ketones on water [1, 2] may help to explain some of the phenomena of dye adsorption by cellulose acetates.

It is well known that the suitability of a dye for cellulose acetate fibres is closely connected with low ionising power. Thus the disperse dyes, which have polar, but not ionic, groups, dye all forms of cellulose acetate, whereas dyes having an ionisable group do not dye cellulose triacetate satisfactorily. They dye the normal secondary acetate well if they have only a weakly ionisable group (e.g. sulphate, $-O\cdot SO_3Na$) in their molecules, but not if the strongly ionisable sulphonate group ($-SO_3Na$) is present. This fall in effectiveness of dyes with increasing ionisation has usually been attributed to their inability to bond to cellulose acetate because they are too firmly held in the water.

It has now been found that strongly ionised dyes, which are not adsorbed by cellulose triacetate as a fibre, are readily adsorbed by it when it is present as a monolayer on water. The monolayer expands in presence of a dissolved ionic dye, but it is apparently unaffected by a highly substantive disperse dye.

The following hypotheses are suggested to account for these facts—

(*a*) The ionised dyes are adsorbed by penetration between the acetate groups in the monolayer, the ionic groups remaining dissolved in the water below.

(*b*) The disperse dye is adsorbed flat against the underside of the acetylated glucose rings in the monolayer, so that the latter is undisturbed in area. (This is similar to the behaviour of tanning substances with protein monolayers [3].) The ionised dyes are unable to take up this orientation on account of the interference of the solvated water they carry.

(*c*) The proportion of water-accessible non-crystalline regions in cellulose triacetate fibre is so low that if a dye can penetrate only those regions it is of no practical value. To produce an adequate coloration the dye must also penetrate some of the more crystalline regions, which it can do only by swelling the structure through breakage of inter-chain polar (e.g. hydrogen) bonds. For this to occur there must be high affinity arising from "multiple-point" dye-to-polymer attachment by several bonds per dye molecule. If an ionised group is present its accompanying solvated water prevents the necessary close approach of dye and

triacetate chain, and "dyeing" is confined to the amorphous regions.

It will be seen that this adsorption mechanism is very similar to the early theories of "solid solution" proposed for cellulose acetate dyeing.

Results of measurements of the difference in expansive effects of dyes with monolayers of cellulose triacetate and cetyl acetate, and of long-chain ketones, are consistent with high polar and low non-polar attraction between dyes and cellulose acetates.

A fuller account is given elsewhere [2].

Note added in Proof

Since this communication was written Tilak and Rao [4] have reported certain properties of non-planar quinonoid dyes having a phenylene nucleus oriented perpendicular to the longest axis of the molecule, in comparison with those of closely related planar dyes. They observe that the planar dyes are substantive to cellulose when used as vat dyes and to cellulose acetate when used as disperse dyes, but the non-planar ones are not substantive to either material.

The behaviour of these compounds with cellulose acetate appears to be in accordance with the above hypothesis of a "multipoint" dye–fibre association, the absence of substantivity of the non-planar compounds being due to the steric effect suggested to account for the non-substantivity of ionised dyes. It may also be remarked that the dichroism observed with dyed oriented cellulose acetate fibres [5,6] is consistent with this form of association.

A. Cameron*
C. H. Giles
T. H. MacEwan

Colour Chemistry Research Laboratory
Department of Chemical Technology
Royal College of Science and Technology
Glasgow C.1

10th September 1957

[1] Allingham, Giles, and Neustädter, *Discussions Faraday Soc.*, (16), 92 (1954).
[2] Cameron, Giles, and MacEwan, *J.C.S.*, 4304 (Oct. 1957).
[3] Ellis and Pankhurst, *Discussions Faraday Soc.*, (16), 170 (1954).
[4] Tilak and Rao, *Chem. and Ind.*, 1320 (5th Oct. 1957).
[5] Preston, Jackson, and Nimkar, *J.S.D.C.*, **65**, 483 (1949).
[6] Vickerstaff, *The Physical Chemistry of Dyeing* (Edinburgh and London: Oliver & Boyd. 2nd edition 1954).

* Present address—Coal Research Station, C.S.I.R.O., Chatswood, Sydney, N.S.W., Australia.

Notes

Meetings of Council and Committees
October

Council—No meeting

Publications—22nd

Colour Index Editorial Panel—3rd, 17th, and 31st

Finance and General Purposes—30th

Death

We regret to report the loss by death of Mr. Percy Andrew.

Leeds Junior Branch

The following officers and committee members have been elected for the 1957–1958 session—

Chairman	Dr. C. B. Stevens
Vice-chairman	Mr. C. L. Bird
Honorary Secretary	Mrs. J. M. Firth

Committee

Mr. J. Budding	Mr. G. J. Morton
Mr. J. Fitzmaurice	Mr. P. Wainwright

Teaching Aids

A Teaching Aids Subcommittee has recently been formed by the Science Masters' Association to collect information concerning teaching aids and to prepare lists of these for circulation to its members. It would be appreciated if representatives of industrial organisations would supply the Subcommittee with the details of any booklets, wall-charts, models, showcases, filmstrips, etc. they may have which would be of use to schools. The details should include the name of the teaching aid, type, cost, etc., and be sent to the Secretary at 24 Coniston Road, Bromley, Kent.

International Symposium on Macromolecular Chemistry

An International Symposium on Macromolecular Chemistry, covering the physics and physical chemistry of high polymers and polymerisation reactions, was held in Prague under the auspices of the International Union of Pure and Applied Chemistry and the Czechoslovak Academy of Science during 9–15th September 1957. Institutions in over twenty countries were represented, and over 150 papers were presented, as well as lectures reviewing recent developments in particular fields. In a short account it is possible only to mention some which may be of particular interest to readers of this *Journal*.

A large number of papers were concerned with polymerisation processes leading to the production of fibre-forming polymers, including the polymerisation of acrylonitrile (Grobe and Spode—Tetlow-Seehof; Bensasson and Bernas—Paris; Edelman—Berlin), acrylamide (Parrod and Elles—Strasbourg), polyamides and related polymers (Kriessink, van der Want, and Staverman—Delft; Hermans, Herkens, and van Velden—Utrecht; Saunders—Pontypool), and polyesters (Griehl and Schnoek—Tetlow-Seehof; Conix—Mortsel). Professor Zeigler gave a review lecture on the use of organometallic catalysts in the production of isotactic polymers, and papers dealing with such polymers were contributed by Overberger, Goodman, and Mark (Brooklyn), Korotkov (Leningrad), and Topchiev and Krentsel (Moscow). A group of papers were concerned with depolymerisation (Grassie and McNeill—Glasgow; Kraliček and Šebenda—Prague; Smith—Pontypool).

Papers on polysaccharides included the consideration of some new esters of cellulose (Rogovin — Moscow), the determination of molecular weights of celluloses (Marx— Mainz; Meyerhoff— Mainz), and the phase structure of cellulose (Mikhailov— Moscow). In a section concerned with proteins and nucleic acids Huggins (Rochester) discussed the principles of protein structure and proposed that in α-keratin polypeptide chains are grouped into triplets, triple triplets, and 27-chain groups to give the most efficient packing of side-chains, and Waldschmidt-Leitz (Munich) discussed the structure of silk fibroin. Kargin (Moscow) considered phase transitions in polymers generally. Among a number of papers dealing with solution properties of polymers may be mentioned contributions on the viscosity of solutions of poly-ε-caprolactam (Rynnikar— Gottwaldov), fractionation (Mussa— Turin; Broda— Lodz), and thermodynamic properties of solutions of cellulose derivatives (Moore— Bradford).

A feature of the Symposium was the simultaneous translation of contributions into English, French, German, Russian, and Czech and the reception of such translations by means of headphones incorporating small transistor radio receivers. Considerable care was taken to ensure adequate discussion. Contributions to discussion and the original papers will be published in the *Journal of Polymer Science*, and review lectures in a special volume to be issued by the Czechoslovak Chemical Society.

W. R. Moore

New Books and Publications

The Science of Color

By the Optical Society of America, Committee on Colorimetry. Pp. xiii + 385. New York: Thomas Y. Crowell Co. 2nd printing 1954. Price, $7.00 or 63s. 0d.

The Optical Society of America in 1933 appointed a committee to revise and expand a report on colour which had been published in 1922. The 1922 report was "designed to set forth a clear terminology in the field of colorimetrics; to summarise the available physical, psychophysical and psychological data relating color to its stimulus conditions; to outline briefly the principal methods of color measurement; and to establish the relationship between their respective scales." This book is the final report of the 1933 committee, and it was first published in 1953. Eleven of the fourteen members of the committee appointed in 1933 were still members of a larger committee when this report was issued twenty years later, and the Chairman had served also on the 1922 committee. It would be expected from this continuity of membership and also from the list of well known names of committee members that an authoritative document on colour would result, and this has been achieved.

There is a great deal of interesting information for the non-specialist, and an attempt has been made in the layout of material to "attract and hold the attention of casual readers." This inevitably means that there is some material of an elementary nature and also some superficial remarks and explanations, but these are mostly confined to the early sections.

The first section deals with the use of colour from the earliest times to the present day, the rather disarming title being *From the Art of Coloring to the Science of Color*. This interesting account can be easily read by the layman. Succeeding sections deal with the concept of colour, physiology, psychological and physical concepts, psychophysics of colour, colorimetry, and colorimeters. The final sections are written in considerable detail and give a very adequate coverage of the quantitative methods of colorimetry.

One of the best features of the book is the comprehensive list of references, which appears to cover publications up to 1951. Thus, while the newcomer to colour is led gently on, the specialist has guidance to further reading from the references, which are arranged in order of sections. As many as 225 references are allotted to the section on *Sensory Aspects of Color*.

Many tests for colour vision are included in this last mentioned section, and it is stated that the repeated taking of a colour vision test tends to improve the individual's score. This does not mean, however, that his basic colour vision has been improved. Since drugs are known which impair colour vision, it is hopefully suggested that drugs may be discovered which will improve it.

On the instrumental side, commercial spectrophotometers are mentioned briefly, the principles of operation of each being given but with no indication of their relative merits. Colorimeters are dealt with in some detail, and an important distinction is made between colorimeters and colour comparators. The latter are instruments used in chemical analysis for comparing a sample with a standard, usually by transmission, and confusion would be avoided if the term *colorimeter* were reserved for instruments which actually measure colour.

Very few errors have been noticed, although there is a prominent printing error near the foot of p. 227.

The psychological aspects of colour are very well discussed, and who would disagree with the following— "Dyers may become strongly attached to certain colours which are fast compared with others which are fugitive"?

This is an admirable book both for the practical man, who wishes to learn underlying principles and methods of measurement, and also for the colour specialist. It is well produced, the 25 colour plates being of high quality, and the price is reasonable.

It is a pleasure to be able to recommend it to all members of this Society.

J. C. GUTHRIE

Textbook of Polymer Chemistry

By Fred W. Billmeyer, Jr. Pp. viii + 518. New York and London: Interscience Publishers. 1957. Price, $10.50 or 80s. 0d.

Although a number of books on polymer chemistry have been published in the past ten years, these have generally been intended for the postgraduate or research chemist, and few, if any, books primarily designed for the undergraduate or advanced student have appeared. This book, however, is intended for the student with some training in organic and physical chemistry and in elementary physics and mathematics. It assumes no prior knowledge of high polymers and includes brief discussions of some physical and physico-chemical concepts necessary for the understanding of the text.

The book is divided into six parts. The first of these constitutes an introduction and includes consideration of the structure and properties of polymers and a historical survey of their investigation and utilisation.

The second part deals at some length with the physical chemistry of polymers. An account of chemical bonds and molecular forces is followed logically by consideration of crystallinity and orientation, phase transitions, and X-ray and infrared methods of studying structure. Treatment is brief but clear. Chapters on thermodynamic principles as applied to polymers and polymer solutions, however, may require considerable elaboration unless the reader is familiar with thermodynamics. Rather more complete accounts of solubility and fractionation are given, and four chapters deal in some detail with such methods as osmotic, light scattering, viscosity, and sedimentation which may be used to obtain information on molecular weights and chain configuration. Under physical chemistry are also included brief but clear accounts of the rheology and the elastic and viscoelastic properties of polymers.

The third part provides condensed accounts of linear and three-dimensional condensation polymerisation, kinetics and absolute reaction rates in addition polymerisation, the thermochemistry of polymerisation, copolymerisation and the structure and composition of copolymers, reactivities and structures of monomers and radicals, diene, divinyl, emulsion, and ionic polymerisations. The significance of rate and molecular-weight data in relation to kinetics and the subject of polymer degradation are also briefly but fully considered.

Part IV, dealing with the properties of plastics, begins with a useful outline of polymer processing and then considers polystyrene and related polymers, acrylic resins, vinyl polymers, polymers containing fluorine and chlorine, ethylene polymers, cellulose plastics, silicones, and miscellaneous resins. Brief accounts are given of their preparation, and rather fuller accounts of structure and properties.

Parts V and VI are shorter and concerned with fibres and elastomers respectively. A general discussion of the structure and the properties of fibres is followed by brief accounts of natural fibres, the conversion of polymers to fibres, cellulosic fibres other than cotton, polyesters, polyamides and related fibres, and vinyl and miscellaneous fibres. A brief consideration of fibre aftertreatments is included. Readers of this *Journal* may consider the space devoted to fibres small, but it is probably adequate in relation to other aspects of the subject. Accounts of the structure and the properties of elastomers are followed by chapters on natural rubbers, related polymers, and synthetic rubbers. The book concludes with appendixes listing symbols used, physical constants, and trade names. There are adequate author and subject indexes.

Lists of well chosen general and specific references, up to the end of 1956, are given at the end of each chapter, so that knowledge of a particular aspect can be extended. There are many clear diagrams and tables. Practical aspects are not lost sight of, and uses and applications are given. Treatment is concise, and generally from the point of view of the physical chemist or the physicist. Organic aspects may require supplementing by other texts. This apart, the book provides a good textbook of polymer chemistry and should be particularly useful for students preparing for Section II of Paper A of the A.S.D.C. examination. The price, although perhaps not high for a book of this type, may, however, deter some from buying it.

W. R. MOORE

Jahrbuch der Textilveredlung Band 3

Edited by Gerhard Meier. Pp. 932. Berlin: VEB Verlag Technik. 1956. Price, DM 35.00.

This volume follows the pattern set in previous years (cf. J.S.D.C., **72**, 103 (1956)). The first 112 pages are devoted to articles, commencing with brief accounts of Wolcrylon (an acrylic fibre) and Trelon (a fibre made from mixed polyamides). Then comes a survey of fluorescent brightening agents (pp. 29–54). This contains a most useful account of the chemistry of these agents, but unfortunately the author (K. Löffler), as he makes clear, was at a disadvantage in not having access to information about British and American commercial products nor to much of the British and American literature. Nevertheless, this article should not be overlooked by those interested in this subject. This is followed by an account of the use of the Pulfrich photometer and a reprint of the lecture on machines for high-temperature dyeing given by Thies to the Society's Huddersfield Section, due acknowledgment being made. The use of metal-complex dyes in wool dyeing is briefly surveyed, and then follows an account of the use of acid and metachrome dyes on Perlon staple fibre. This section of the book concludes with a brief survey of the Acramins (FBy).

The second section of the book consists of 391 pages dealing with the fibres, auxiliaries, dyes, and machinery developed by some German, some Swiss,

and one Czech firm. There appears to have been neither rhyme nor reason used in choosing the firms whose products were to be dealt with; e.g. only three of the five Swiss dyemakers are mentioned, and with one exception all the machinery makers mentioned come from the zone of Germany dominated by Russia. The information given simply reproduces what is already available in the pattern cards, the maker's reference number to which is given in most cases. It is hard to see what justification there is for the assembly of this information in this form. This is followed by a table listing 1134 auxiliary agents (German 1100, Swiss 34, rest of the world nil), giving the name, maker, chemical basis, use, and in many cases some properties of each product. This is probably the part of the book that will be of most use, especially to readers outside Germany.

The survey of the literature and patents for 1953–1954 lists some 6502 items and occupies 350 pages. Articles and books are listed separately, being arranged in each case alphabetically according to their authors' names, anonymous material being placed last. Patents are listed numerically by countries. There is a subject index to these lists. No critical comment is given, but only the bare titles, and it is difficult to see why such a list should have been regarded as worth publishing. Finally there are indexes to the dyes and auxiliary agents mentioned in the book and a general subject index.

With the exceptions mentioned above, there is little that is new or worth attention in this book, the larger part of which consists of a reproduction of trade literature. The larger reference libraries will have to have it on their shelves for the sake of completeness, and it is there that the practical dyer and finisher should seek it on the rare occasions when it will be of use for him to consult it.

C. O. CLARK

Studies in Ancient Technology
Volume IV
[History of the Textile Fibres and their Processing in the Ancient World]

By R. J. Forbes. Pp. vii + 257 with a frontispiece and 36 figures and 7 tables. Leiden, Netherlands: E. J. Brill. 1956. Price, 20.00 florins.

This book is an attempt, and let it be said right away an excellent and successful attempt, to summarise present knowledge of the techniques of textile processing used in the ancient world, i.e. up to and including classical Roman times. It is divided into seven sections—(1) The Fibres and Fabrics of Antiquity, (2) Washing, Bleaching, Fulling, and Felting, (3) Dyes and Dyeing, (4) Spinning, (5) Sewing, Basketry, and Weaving, (6) Weaving and Looms, and (7) Fabrics and Weavers.

It is, of course, the second and third sections which are of most interest to members of the Society and to which they will almost certainly first turn. The meagreness of our knowledge of how the ancients cleansed and finished their cloths is indicated by the fact that the second section occupies only 17 pages. Our knowledge of ancient dyes and dyeing is greater, and the section dealing with them occupies 50 pages; nevertheless, our knowledge of these matters is still far from complete or exact.

The author has done his work well, though at times he is, perhaps, a little inclined to be too definite in his statements. The able way in which he has summarised the knowledge to hand is shown by the wealth of references. The book is most readable and cannot fail to be of absorbing interest to anyone engaged in any branch of the textile industry. Certainly, anyone working on the history of any section of textile processing or on the history of dyes will be bound to consult this work, if only because of its literature references. There is one minor flaw, which, however, does not detract from the merit of the work, viz. the use of words and phrases not used by anyone whose mother tongue is English, e.g. "musea" for *museums*, "dye-shops" for *dyehouses*, "uncovered" for *discovered*, or a phrase such as "The Spartans are reported to have chased the dyers from their country as they robbed wool from its beautiful natural white hue". When the second edition of the book is being prepared, and one will most probably be called for some day, it would be as well to have it edited for its English, preferably by someone connected with the textile industry. A special word of praise is due to the publishers for the way in which they have produced the book, which is a pleasure to look at and handle.

C. O. CLARK

Organic Analysis
Volume 3

Edited by John Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger. Pp. viii + 546. New York and London: Interscience Publishers. 1956. Price, $11.50.

The above editors and their contributors got away to a fine start in 1953 with Volume I in this series of monographs. Such is the rate of growth in every department of science, however, that time is the increasingly menacing enemy of the textbook writer; this position can only worsen with the passing years. The first three volumes have appeared in 1953, 1954, and now 1956, and even if only one further volume is intended to complete the series (the overall intention is not disclosed either on or in the books), the end will no sooner come than it will be time to consider the revision of Volume I. Conscientiously executed, a series such as this must now resemble the task of painting the Forth Bridge—no sooner completed than recommenced. The day must surely come when the textbookwise documentation of each facet of science will be comparable with the nightmare of Beilstein.

The series as a whole is designed to cover the field of organic analysis, from the standpoints of functional group analysis and the use of modern techniques. This latest volume falls into the following sections (authors' names in parentheses)—organic acids (Mitchell, Montague, and Kinsey—any relation?), acid anhydrides (Hammond), amines and amides (Hillenbrand and Pentz),

olefinic unsaturation (Polgár and Jungnickel), analytical mass spectrometry (Dibeler), and synthetic organic coating resins (Shreve). The value of this volume as a mere review, and it would be ridiculous to suggest that it is not very much more than that, is indicated by the number of references to the literature: there are 1383 in all, no less than 698 relating to the determination of olefinic unsaturation. This is a sharp reminder of the passage of time to anyone whose reflexive thought on hearing the term *olefinic unsaturation* is "hydrogenation or halogenation".

The usefulness of the earlier essays to the chemist who is concerned with dye or surfactant intermediates will be obvious, as will that of the essay on olefinic unsaturation to the paint chemist. This latter is classic in its thoroughness and magnitude, and in many ways is the outstanding achievement of the book. A very good feature of the book is the systematic approach that is listed at the beginning of each monograph. The case of olefinic unsaturation will serve to illustrate this: it is divided into twenty sections— *Introduction*; *Chemical Methods*: halogenation, hydrogenation, oxidation, nitration, sulphuric acid absorption, thiocyanation, addition of metal salts, addition of maleic anhydride, other chemical methods; *Instrumental Methods*: infrared absorption, Raman spectroscopy, ultraviolet absorption, mass spectrometry, polarography, other physical methods; *Chromatographic Methods*: adsorption chromatography, partition chromatography; *Recommendations*— in which the methods recommended for the determination of unsaturation in various types of compound are given and commented upon in a six-page table. The above sections have, in all, 28 additional subsections.

The inclusion of a section dealing with the analysis of organic coating resins is most welcome; many papers have been published in this field, mostly concerned with specific determinations or with "group analytical" procedures, and a review is overdue. Unfortunately, this is perhaps the least successful section of the book. The bibliography, even though it contains 148 references, is far from complete, the range of interest is confined by the persistent recurrence of rosin, and in these days a better example could have been selected to illustrate a complete analysis than that of a nitrocellulose lacquer. Strangely enough, there is strong emphasis on the infrared spectroscopic determination of both single and mixed resins— this is to be applauded, though one feels that such instrumental methods are not yet as commonly used here as in the U.S.A.

The text is clearly printed, error-free, on good paper, and the binding is equal to the manhandling that the book is certain to have in the possession of all analysts; its purchase cannot be neglected by any serious analyst concerned with any field touched by its contents— and there are precious few that are not.

J. W. Duarte

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

Machinery for High-temperature Dyeing
H. Eberhard
S.V.F. Fachorgan, **12**, 374–381 (June 1957)
High-temperature dyeing machinery for the dyeing of loose stock, sliver, and packages (both bulk and laboratory work) is described and illustrated. B.K.

High-temperature Piece-dyeing Machinery
H. U. Schmidlin
S.V.F. Fachorgan, **12**, 384–398 (June 1957)
The Barotor, Benninger pressure jig, Smith pressure jig, Burlington beam-dyeing machine, and the Colorfix universal high-temperature dyeing machine are described and illustrated. B.K.

Continuous "Mercerisation" of Cellulose
V. A. Gruzdev
Tekstil. prom., **17**, 58–60 (April 1957)
Machinery (manufactured by Sands Werkstader) for the continuous formation of alkali cellulose is appraised critically. G.J.K.

PATENTS

A Two-zone Dryer
H. Orth and E. Haag *BP* 781,154
Wet material, e.g. salt containing 5% moisture, is charged on to an air-permeable surface and stirred mechanically whilst hot air is blown through the material from beneath. As the material becomes drier, it is carried by the air stream, through a gate-valve, into a second chamber where it is dried to the desired degree. E.S.

Thread-advancing Reels
Celanese Corpn. of America *BP* 777,522
The efficiency of liquid treatment on a thread-advancing reel can be improved by simultaneously squeezing the yarn and applying suction between successive points of application of liquid. W.G.C.

Heat Moving Threads
N.V. Onderzoekingsinstituut Research *BP* 779,800
Threads are guided round a stationary heated rod according to a helical line with an angle of inclination of $> 70°$, and preferably 85–89°. This enables the threads to be moved with a minimum of tension. W.G.C.

Steaming of Hanks
E. E. Bellmann, R. Kronsbein, and F. Bellmann
BP 776,103
Apparatus in which the hanks are steamed under tension and simultaneously rotated. C.O.C.

Washing Machine
S. Newbery *BP* 777,854
A drum machine has hollow perforated baffles connected to an annular reservoir fitted at one end of the drum. Liquor pumped from the machine to the reservoir is thereby sprayed on to the goods during rotation of the drum. G.E.K.

Dyeing at 100°C. or over
Groeninghe Ververij *BP* 776,983
A closed circulating system in which dye liquor at 100°c. or more is circulated under static pressure through the material. C.O.C.

Hank Poles for Dyeing Machines
Freeman Taylor Machines *BP* 776,563
An extensible pole which is readily cleansed by being flushed through from end to end. C.O.C.

Vats, Becks, etc.
Richard Farnworth & Co. *BP* 776,068
An open-topped inner shell is surrounded by a closed-topped outer shell, the walls of the shells being nowhere in

contact. This provides a space all round the sides and over the top of the inner shell. Steam is led from outside into this space to heat the contents of the inner shell. This arrangement is particularly suitable for mixing pans, e.g. for starch. C.O.C.

Supporting and Conveying Web-like Materials
AB Svenska Fläktfabriken *BP* 777,250
Means for preventing fluttering of the material when being fed to and through a drying machine. C.O.C.

Treating Warps or Fabric
Gebruder Sucker *BP* 781,269
Where cloth etc. passes through an input and later through an output set of rollers, the speed ratio of the two sets of rollers being variable, control means are provided to automatically correct any deviations arising in this ratio from the desired constant value. C.O.C.

Wet Treatment of Sheet Material
Martini & Cie, Bleicherei, Farberei, Druckerie u. Appretur-Anstalt *BP* 776,406
The material while passing through the treating liquid, goes through a nip placed below the surface of the liquor. This nip is formed by a roller covered with an elastic material which is either porous or else is coated with a porous material and a counter-pressure roller. This gives very gentle yet uniform and intensive treatment. C.O.C.

Device for obtaining very even Liquid or Gaseous Treatment of Fibrous Materials
Maschinenfabrik Benninger *BP* 781,174
A hollow cylinder is mounted across the vessel or chamber containing the treating medium, being placed below the surface of the medium and transversely to the line of travel of the material being treated. The cylinder has two opposed longitudinal slits; so that the material can pass through it, each of these slits has outwardly directed flanges. The cylinder is mounted so that it oscillates about its axis when the material to be treated passes through it. This oscillation induces movement in the treating medium and may or may not cause movement of the material being treated. This results in very even treatment of the material. The principle is applicable to both liquid and gaseous treatments. C.O.C.

Heated Cylinders, Rollers and the like
Spooner Drier & Engineering Co. *BP* 778,232
Water is circulated through the cylinder and heated by direct steam. C.O.C.

Drying of Textiles
Samuel Pegg & Son *BP* 781,606
The material is placed in a closed circuit through which air is passed at $\geq$ 10 lb. per sq.in. pressure. The air is heated before it reaches the material and is cooled after leaving it to condense entrained moisture before returning to the heating zone. The condensate is drawn off by a valve which opens automatically when sufficient condensate has collected in its vicinity to prevent air passing through it. C.O.C.

Cylinder Drying Machine
Sir James Farmer Norton & Co. *BP* 779,093
A machine of greatly increased output has hot air nozzles placed in a casing around each drum. One side of the cloth contacts one drum and the other side the next drum so that both sides of the cloth are dried. Each casing both receives hot air and leads the exhausted air away. C.O.C.

Drying or Conditioning Web-like Material
AB Svenska Fläktfabriken *BP* 776,141
An improved method of circulating the air in a tenter or similar drying machine. C.O.C.

Tenter
E. Gordon Whiteley *BP* 776,236
A machine which takes up less space than previous machines of the same capacity. C.O.C.

Silk-screen Printing Apparatus
D. M. Johnson *BP* 778,380
A small and cheap device for raising and lowering the screen from the carrying to the printing position and for moving it from one printing position to the next. C.O.C.

Silk-screen Printing Machine
Argon Service *BP* 777,022
A machine which is readily adjusted to print material of many different thicknesses, widths and lengths. C.O.C.

Ager
R. P. Higginbottom *BP* 779,149
A three phase heat exchange unit for an ager consists of a rotary cylinder which gives (*a*) a hot dry phase at each end (at steam temperature), (*b*) a cool wet phase (the centre section) (maintained as a heat exchanger at $< 212°$F.), and (*c*) a merger phase between the hot and cool phases where the moisture tapers off from the cool to the hot phase. Such units supply moisture to facilitate fixation of the print or discharge. Control of conditions can be established throughout the length of the ager by suitable distribution of the units. Superheating of steam is prevented and completeness of reactions facilitated. A smaller ager can be used as the reactions are speeded up. A very marked increase in colour value is obtained. Often more than one fabric can be processed simultaneously over the same guide rolls as for a single fabric. C.O.C.

Raising Machine
A. Monforts *BP* 777,461
A machine in which the speeds of the drum, the raising rollers and the fabric are interdependent and can be accurately adjusted to produce any required degree of raising. C.O.C.

Application of Substances to Carriers under the Influence of Fields of Force Generated Between the Substances and the Carriers
Saladin & Co. *BP* 779,351
Means to ensure the particles of the substance to be applied, e.g. fibres, paint or metals, do not become electrically charged. C.O.C.

Nylon Hose Preboarding
Mellor Bromley & Co. *BP* 777,828
A vertical cylindrical retort is accessible from two opposite sides for receiving alternately two form-carrying carriages propelled along rails extending outwards from each side of the chamber. The chamber is closed by doors rotating on the inside, prior to the steaming period. Hot air circulation is provided for drying the hose after steaming. G.E.K.

Compressive Shrinking of Fabrics (X p. 529)

II—WATER AND EFFLUENTS

Use of Activated Silica in Water for Textile Finishing
F. A. Prisley
J. Amer. Water Works Assocn., **49**, 459–463 (1957): *Chem. Abs.*, **51**, 10800 (25 July 1957)
Use of activated silica increases speed of formation as well as size, density, and strength, of the alum floc. Cl_2 is used to activate the silica. The resulting floc settles rapidly. C.O.C.

Dialysis of Caustic Textile Wastes
N. L. Nemerow and W. R. Steele
Proc. Ind. Waste Conf. 74–81 (1955): *Chem. Abs.*, **51**, 8443 (10 June 1957)
Waste caustic liquor from vat dyeing is recovered by concentrating to 38–40% by evaporation and dialysis through mercerised parchment paper. The caustic is recovered as a relatively pure 10–12% solution. The discharge contains 2–3% NaOH and 70–90% of the impurities. Return on investment for evaporation and dialysis usually exceeds 50%. C.O.C.

Waste Water from Leather Factories
H. Scholtz
Österr. Wasserwirtsch., **8**, 319–325 (1956): *Chem. Abs.*, **51**, 10935 (25 July 1957)
The chemical composition and neutralisation of waste water from leather manufacture is discussed. C.O.C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Constitution of Maize Starch Dextrin
J. D. Geerdes, B. A. Lewis, and F. Smith
J. Amer. Chem. Soc., **79**, 4209–4212 (5 Aug. 1957)
Study of periodate oxidation and methylation of fractioned maize starch dextrins led to the conclusion that dextrinisation is accompanied by considerable transglycosidation and development of a highly branched structure. C.O.C.

Triethylenediaminezinc Hydroxide Solutions as Cellulose Solvents
G. Jayme and K. Neuschäffer
Das Papier, **11**, 47–51 (1957): *Chem. Abs.*, **51**, 8429 (10 June 1957)
Under suitable conditions cellulose dissolves in $(CH_2NH_2)_2$ containing $Zn(OH)_2$ to yield colourless solutions. The solvent contains 3 mol. $(CH_2NH_2)_2$ to 1 mol. $Zn(OH)_2$. C.O.C.

Mothproofing Agents. XXIII—Synthesis of Compounds Analogous to Mitin FF
K. Matsui, K. Oda, and J. Seino
Yûki Gôsei Kagaku Kyôkai Shi, **14**, 401–6 (1956)

XXIV—Azo Dyes derived from 3:3′:5:5′-Tetrachloro-2:2′-dihydroxy-4″-aminotriphenylmethane-2″-sulphonic Acid
K. Matsui, K. Watanabe, and K. Hagihara
Ibid., 466–471: *Chem. Abs.*, **51**, 10414, 10415 (25 July 1957)
XXIII—Synthesis of products analogous to Mitin FF is described and their mothproofing efficiency given, only one was as efficient as Mitin FF.
XXIV—Syntheses of several azo dyes are described and their fastness to light and washing and their mothproofing efficiencies measured. None of them has greater mothproofing efficiency than Eulan N. C.O.C.

PATENTS

Improving the Foaming Power of Anionic Detergents
California Research Corpn. *BP* 783,318
When low mol. wt. *p*-acylphenyl glycol ethers are added to a mixture of a C_9–C_{16} monoalkylbenzene sulphonate, and an organic sulphate or sulphonate containing a C chain of 14–18 C, they impart ability to produce copious foam which is stable to mechanical agitation. C.O.C.

Salts of Hydrazine
Genatosan *BP* 781,491
The products formed by treating hydrazine or its salts with aliphatic amino polycarboxylic acids which act as chelating agents, are useful *inter alia* for the simultaneous softening and deoxygenation of water. C.O.C.

Hardenable Ternary Condensates from Aminotriazines
Ciba *BP* 778,204
1 mol. of a formaldehyde condensate of an aminotriazine compound or an ether thereof with an aliphatic alcohol of < 5 C is condensed with 1–3 mol. of an aliphatic compound containing a chain of > 6 C and a reactive H atom bound to O, S or a non-basic N atom. The resulting compound is then reacted with 1–2 mol. of a monohydroxy- or monomercapto-monocarboxylic (or sulphonic) acid. The products have wide uses as hardenable resins for textile finishing. C.O.C.

Amino Triazine–Formaldehyde Condensates—Water-repellent Finishes
Ciba *BP* 781,265–7
Preparation of formaldehyde condensates of amino-1:3:5-triazines containing at least 2 NH_2 groups and residues of high mol. wt. is described. They are used in textile finishing, particularly in the production of water-repellent finishes which resist washing at the boil. C.O.C.

Non-chlorine Retentive Resins for Textile Finishing
Cluett, Peabody & Co. *USP* 2,738,292
The resin obtained by reacting together acetone, formaldehyde and acrolein in presence of an alkaline catalyst, when applied to cellulosic fibres, particularly those of regenerated cellulose, imparts excellent progressive dimensional shrinkage control without loss in tensile strength or damage caused by chlorine retention. C.O.C.

Acetal Condensates for Dimensional Control of Textiles and Paper
Quaker Chemical Products Corpn. *BP* 776,468
The water-soluble polymer obtained by condensing a polyalkylene glycol containing 2–4 alkylene groups with an aldehyde in presence of an acid catalyst can be used to impart dimensional stability to textiles and paper. Thus diethylene glycol and paraformaldehyde are heated in toluene under reflux with sulphuric acid as catalyst, to yield a product completely soluble in water and toluene. Cellulose fabric is padded with an aqueous solution of this product containing an acidic catalyst, dried and then baked at > 120°c. for 30 sec.–10 min. The treated fabric is resistant to progressive shrinking on being laundered in boiling soap solution. C.O.C.

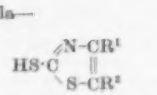
Quaternary Ammonium Salt Derivatives of Silicon Compounds as Finishing Agents for Cellulosic Textiles
Deering Milliken Research Corpn. *USP* 2,738,290
Compounds of formula—

$$R_nSi[-Y-N(tert.)X]_{4-n}$$

(n = 1, 2 or 3; R = satd. Alk or aralkyl of 1–10 C; Y = bivalent aliphatic radical of 1–10 C; N(*tert.*) = residue of a (tertiary amine) are used to impart water repellency and/or softness, dimensional stability, flame resistance and crease recovery to textiles. Thus rayon cloth is treated with a 5% solution of octadecyldimethylsilyldodecamethylene pyridinium fluoride in 5% aq. pyridine, dried at 55°c., and baked for 15 min. at 150°c., rinsed and dried. The treated cloth is water repellent and dimensionally stable even after repeated washings and dry cleanings. C.O.C.

αα′-Dihalogenodicarboxylic Acids for restoring the Cross-linkages of Reduced Keratin
DuP *USP* 2,739,033
αα′-Dichloro(or bromo)dicarboxylic acids are excellent agents for cross linking reduced keratin. Thus dyed wool is stripped by treating it with a mixture of *αα′*-dibromosuccinic acid and sodium hydrosulphite, there being little shrinkage or loss in tensile strength. In another example hair is permanently waved by treating it first with thiosorbitol and then with the disodium salt of *αα′*-dibromosuccinic acid. C.O.C.

Agents for Bonding Rayon and Nylon to Natural and Synthetic Rubbers
Monsanto *BP* 776,910
Compounds of formula—



(R^1 = H or Alk of 1–4 C when $R^2 = -(CH_2)_nCO{\cdot}NH_2$ (n = 0–4) or *vice versa*), e.g. a 2-mercapto-4-methylthiazole 5-carboxylic acid halide, are used. C.O.C.

Monoazo Compounds of Strong Absorption of Ultraviolet Radiation
ICI *BP* 783,325
Compounds of formula—

AN:N·C(COO Alk)HX

(A = benzene containing at least one negative substituent; X = CN, $COCH_3$ or COO Alk), e.g. diethyl-3-chloro-4-methyl-6-sulphophenylazomalonate, strongly absorb ultraviolet radiation. Colour photographs washed in an aqueous solution of these products are given much better fastness to light. C.O.C.

Flame-resistant Elastomer Compositions (XIII p. 531)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Relationship between Half-wave Potentials and the Chemical Structures of Azo Compounds. Determination of the Chemical Structure of Two Dyes
L. Moelants and R. Jansen
Bull. soc. chim. Belges, **66**, 209–217 (1957): *Chem. Abs.*, **51**, 10279 (25 July 1957)
The chemical structure of two dyes obtained by chromogenic development of colour couplers of the indazolone type with *p*-dimethylaminoaniline, has been determined from polarographic measurements. C.O.C.

Colour and Constitution
H. S. Bek
Tidsskr. Textiltek, **15**, 57–61 (1957): *Chem. Abs.*, **51**, 10908 (25 July 1957)
The present conception of the relationship between colour and constitution is reviewed on the basis of resonance, conjugation, hyperconjugation, steric hindrance, and extramolecular action. A greatly simplified example of the calculation of the wavelength of maximum absorption is given. The chromophore theory is brought up to date on the basis of modern electronic theory. C.O.C.

Structure of the Primary Condensation Product in the Koenig Dye Synthesis
S. Creyf and L. Roosens
Mededel. Vlaam. Chem. Ver., **19**, 1–11 (1957): *Chem. Abs.*, **51**, 7916 (10 June 1957)
Review, over 40 references. C.O.C.

Mechanism and Kinetics of the Coupling of *p*-Amino-*NN*-dialkylanilines in Aqueous Solution
J. Eggers
Z. Elektrochem., **60**, 987–998 (1956): *Chem. Abs.*, **51**, 8033 (10 June 1957)
Oxidation of p-$H_2NC_6H_4N(C_2H_5)_2$ (I) by excess $K_2S_2O_8$ (II) was investigated kinetically at pH 7. At first the reaction I + II → p-$(C_2H_5)_2NC_6H_4NH$ (III) is rate-determining but soon the reaction II + III → $p(C_2H_5)_2N^+ = C_6H_4 = NH$ (IV) takes over. III is continually being reformed by the reaction of I and IV. Toward the end of the reaction saponification of IV to p-$(C_2H_5)_2N^+ = C_6H_4 = O$ becomes important. Absorption experiments showed that the leuco dye formed from I, III or IV and a p-unsubstituted phenol is oxidised to the dye by IV rather than II. With p-substituted phenols the latter reaction does not occur and the rate of dye-formation is a direct measure of the rate of coupling. IV can couple but III can not. C.O.C.

Monoazo Dyes from Furoylacetarylides and Dibenzothiophene or Dibenzothiophene Sulphone
A. Cerniani
Ricerca sci., **26**, 3089–3092 (1956): *Chem. Abs.*, **51**, 8439 (10 June 1957)
Furoylacetarylide was coupled with 3-aminodibenzothiophene or 3-amino- or 2-aminodibenzothiophene sulphone in 10% NaOH at 0°c. and the dyes recrystallised from chlorobenzene. Using furoylacetarylides having the Ar indicated gave dyes of λ max. p-$CH_3C_6H_4$ 414, 397, 413; p-$C_2H_5OC_6H_4$ 416, 402, 416; 2:5-$Cl_2C_6H_3$ 414, 395, 410; 2-$C_{10}H_7$ 417, 400, 413; benzothiazolyl 417, 400, 412; dibenzofuryl 417, 402, 412. C.O.C.

Synthesis of Surface-active Dyes and their Properties. I and II
O. Yuda
Nippon Kagaku Zasshi, **77**, 896–901 (1956): *Chem. Abs.*, **51**, 9163 (25 June 1957)
Nonylphenol (I) was coupled with sulphanilic acid, and also naphthionic acid and I, decylaniline (II) and Schaeffer acid, II and R-acid, dodecylaniline (III) and Schaeffer acid, III and R-acid, III and G-acid, III and H-acid, III and Koch acid, aniline and G-acid, and toluidine and G-acid, in an effort to prepare surface-active dyes. Their solubilities in water are given together with their absorption spectra in the visible range, surface-tension, electrical conductivity, affinity for fibres, and their effect on the water-repellency of the fibres. C.O.C.

Absorption Spectra of Dyes. I—Aggregation and Absorption Spectra of Benzidine Diazo Dyes
Y. Tanizaki and N. Ando
Nippon Kagaku Zasshi, **78**, 343–348 (1957): *Chem. Abs.*, **51**, 10230 (25 July 1957)
Measurement of the absorption spectra of C.I. Direct Reds 28, 2 and 7 in aq. soln. of 10^{-5}–10^{-3} mole/l. showed that the deviation from Beer's law of these dyes decreased in the order given above. C.I. Direct Reds 28 and 2 showed absorption bands in the long-wave-length range (600–700 mμ), the intensity of which increased with concentration as well as with addition of neutral salts. This is caused by micelle formation. For steric reasons, the micelle formation of these 3 dyes decreases in the order given above in qualitative agreement with the decreasing deviation from Beer's law. C.O.C.

Conjugated Reaction in Interaction of γ-Radiation with Aqueous Solutions of C.I. Basic Blue 9
A. I. Chernova, V. D. Orekhov, and M. A. Proskurnin
Zhur. Fiz. Khim., **30**, 1343–1348 (1956): *Chem. Abs.*, **51**, 10246 (25 July 1957)
The dye solution (0·025–0·00025-M + 0·01-3N-H_2SO_4) was irradiated with an average 30 r./sec. intensity. The dye concentration was determined photometrically. The time of irradiation varied within 60 min. and the maximum dosage to which the solution was exposed was 100 kr./ml. Reversible reduction occurred in presence of N_2 glucose in an atmosphere of N_2, with a yield of 5·2 moles/100 e.v. The reaction is assumed to involve excited water molecules. Oxidation of the dye was brought about by sensitisation with Fe^{+++}, with the yield of oxidised dye 7·8 equiv./100 e.v., whereas the initial yield of reduced Fe proceeded with the yield to 8·2 equiv./100 e.v.; the high yield proves participation of excited water molecules in the reaction. Addition of 0·01 N-$FeSO_4{\cdot}(NH_4)SO_4$ protected the dye from discoloration in air in presence of 3 N-H_2SO_4, whereas there was no protective effect with the same amount of Fe^{++} in presence of 0·8 N-acid. C.O.C.

Reaction of Methylene Blue with Cuprous Chloride in Aqueous Solution
A. A. Kachan
Ukrainian Chem. J., **23**, 325–332 (June 1957)
The reduction of Methylene Blue (characteristic absorption in the ultraviolet at 290 mμ.) by acidified cuprous ion is investigated spectrophotometrically and shows that complete reduction to the leuco form (absorption band at 255 mμ.) does not at first occur. A semi-quinone type of intermediate is suggested. G.J.K.

Photochemical Reactions between Methylene Blue and Tri-, Di-, and Mono-methylamine
H. Obata and M. Koizumi
I. *Bull. Chem. Soc. Japan*, **30**, 136–141 (March 1957)
Methylene Blue in evacuated soln. in H_2O, C_2H_5OH, i-C_3H_7OH, i-C_4H_9OH, $CH_3{\cdot}CO{\cdot}CH_3$ and $CH_3{\cdot}CO{\cdot}C_2H_5$, together with mono-, di- or tri-methylamine is bleached when irradiated with light of wavelength ca. 620 to 720 mμ. The reaction products are the leuco dye and a compound capable of oxidising KI to I_2 and thought to be the amine oxide. The bleached soln. show a slight absorption in the near infrared which slowly decays in the dark. This is attributed to a long-lived intermediate. When triethylamine is in considerable excess of Methylene Blue, bleaching is of the first order with respect to the dye. The following reaction scheme is proposed in aq. soln.—

$$MB + H_2O + (C_2H_5)_3N \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$$

$$\text{Intermediate} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MBH_2 + TAO$$

(MB = Methylene Blue, TAO = Triethylamine oxide)
The results agree with the rate expression—

$$x = Ae^{-(k+\sigma)t} + Be^{-(k-\sigma)t}$$

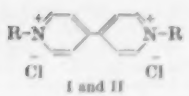
where x = concn. of MB at time t; $k = 1/2\ (k_1+k_2+k_3)$;

$$\sigma = 1/2\ \sqrt{(k_1+k_2+k_3)^2 - 4k_1k_3};\ A = c/2\left(1 + \frac{k_1-k}{\sigma}\right)$$

$$B = c/2\left(1 - \frac{k_1-k}{\sigma}\right);\ c = \text{initial concn. of MB.}$$

II. Idem. *ibid.*, 142–147
The effect of varying conditions on the photobleaching of Methylene Blue are examined and analysed by the rate expression above. It is found that k_1, k_2 and k_3 are not true rate constants, but that $k_1 = k_{1o}[OH^-][(C_2H_5)_3N]I_0$ and k_2 and k_3 are also dependent on light intensity and amine concn. Addition of Fe^{3+} considerably diminishes the value of k_3 and the absorption spectrum of the intermediate becomes more prominent. Cu^{2+} causes an induction period of duration proportional to the concn. of Cu^{2+}. It is considered that Fe^{3+} stabilises the intermediate and Cu^{2+} attacks it. A.J.

Polarographic Behaviour of Viologen Indicators
R. M. Elofson and R. L. Edsberg
Canadian J. Chem., **35**, 646–650 (July 1957)
Methyl- and benzyl-viologen chlorides (I: R = CH_3, II: R = $C_6H_5{\cdot}CH_2$) are reducible at the dropping mercury electrode over the pH range 1–13. Each compound gives two one-electron waves, of which the first in each case has $E_{\frac{1}{2}}$ independent of pH over the whole range and values −0·678 v.vs. S.C.E. for I and −0·592 v.vs. S.C.E. for II, in good agreement with the values for E_0 found potentiometrically. The second wave for I is symmetrical and has $E_{\frac{1}{2}} = -1{\cdot}038$ v. in the pH range 5–13. For II the second wave is irreversible and is followed by two other irreversible waves. The first wave is taken to represent the formation of the unstable radical III and the second wave the isolable compound IV.



I and II

III

IV A.J.

Irreversible Photobleaching of Solutions of Fluorescent Dyes. IV— Photoreactions in Methanol, *iso*Propanol, and Ketones and the General Conclusion for the Photobleaching of Eosin

M. Imamura

Bull. Chem. Soc. Japan, **30**, 249–254 (April 1957)

Rates of photobleaching of soln. of eosin in alcohol–water and ketone–water mixtures have been measured both in the absence and presence of oxygen, and satisfactory rate equations derived. Analysis of the results leads to the conclusion that aerobic photobleaching in soln. containing water is via reaction of the triplet state of the dye with oxygen. A.J.

Effect of Energy Migration on Fluorescence in Dye Solutions

J. Lavorel

J. Physical Chem., **61**, 864–869 (July 1957)

The steady-state distribution of excited molecules in an illuminated liquid showing fluorescence is calculated assuming energy migration by resonance transfer. Equations are derived for the effect of this on the spectral distribution of fluorescence and on the observed action spectrum of fluorescence excitation. A tentative value of the mean displacement between absorption and emission due to resonance transfers is derived from spectral observations on alkaline fluorescein solutions. W.R.M.

Photoreduction of Fluorescein Dyes and Long-lived Excited States

A. H. Adelman

Univ. Microfilms (Ann Arbor, Mich. U.S.A.) *Publ.* No. **18342**, 122 pp. (microfilm $1·65, paper enlargement $12·20)

Light-induced Spectral Shift of Thiazine Dyes in the Bound State

N. Wotherspoon and G. Oster

J. Amer. Chem. Soc., **79**, 3992–3995 (5 Aug. 1957)

Thiazine dyes in presence of polymethacrylic acid or polyacrylic acid undergo a spectral shift when irradiated with visible light. This reaction was followed either at a fixed wavelength or by scanning the spectrum repetitively by a combined recording spectrophotometer and irradiation apparatus. Two photo products are formed, one in absence of oxygen and the other by photooxidation of the first. The rate of formation of the second product is retarded by small amounts of *p*-phenylenediamine or by KI suggesting that long-lived excited states are involved. The final photoproduct is the same for all the thiazine dyes studied and is identical with thionine. The reaction requires a polyacrylic acid but does not take place in presence of other high polymeric acids or dibasic acids. C.O.C.

Thiazoles. XXX— A New Type of Quinoid Thiazole Compound (Thiazole Blue)

H. Beyer, C-F. Kröger, G. Berg, C. Bischoff, and M. Zander

Chem. Ber., **89**, 2230–2239 (1956); *Chem. Abs.*, **51**, 8070 (10 June 1957)

Oxidation of 2-anilino-thiazoles, bis(2-thiazoyl)amines, 2-thiazolylhydrazones and *NN*-diphenyl-*N'*-2-thiazolylhydrazines having a H atom in the 5-positions with $KMnO_4$, CrO_3, PbO_2 or $FeCl_3$ in neutral medium, yields the corresponding substituted 2:2′-diimino-$\Delta^{3,3'}$-5:5′-bisthiozolinylidenes, e.g. 4:4′-diphenyl-2:2′-bis(phenylimino)-$\Delta^{3,3'}$-5:5′-bisthiazolinylidene (violet crystals), 4:4′-diphenyl-2:2′-dioxo-$\Delta^{3,3'}$-5:5′-bisthiazolinylidene bis-(diphenylhydrazone) (blue crystals) and the 4:4′-dimethyl-analogue of the latter (green crystals). The mechanism of these oxidations and the relationship between colour and constitution are discussed. C.O.C.

Synthesis of Coronene Derivatives. I— Carboxylic Acids

H. Hopff and H. R. Schweizer

Helv. Chim. Acta, **40**, 541–549 (May 1957)

The complex formed between carbamyl chloride and anhydrous aluminium chloride has been reacted with varying amounts of coronene at different temperatures and in several solvents. The monoamide was hydrolysed to the carboxylic acid I (m.p. 341°c.), which was converted into the acid chloride, the anilide and the methyl ester. The dicarboxylic II and tricarboxylic acids and their methyl esters were isolated as mixtures of isomers. The dyeing properties of the acylaminoanthraquinone derivatives of I and II were studied. That from II had much better affinity for the fibre than I and had higher tinctorial power. Both dyes gave a redder shade than the corresponding dyes made from iso- and tere-phthalic acids. Fastness properties were not studied. J.E.B.

Indigo Dyes. VI— Optical Evidence of the Reversible Formation of *cis*-Indigo Dyes caused by Irradiation

R. Pummerer and G. Marondel

Ann., **602**, 228–232 (1957); *Chem. Abs.*, **51**, 10236 (25 July 1957)

NN'-Dimethylindigo (I), its 5:5′:7:7′-tetrabromo derivative (II) and *NN'*-diethylindigo (III), when irradiated with orange light showed marked changes in the magnitude of ε at the three absorption maxima. The solvents used were specially purified $CHCl_3$, CCl_4, CH_2Cl_2 and C_6H_6. The original ε at λ max. were determined before exposure and again after 20 min. irradiation at λ 550 mμ. Alterations in ε for I is $CHCl_3$ and CCl_4, III and these and CH_2Cl_2 and II in $CHCl_3$ and C_6H_6 are tabulated and discussed. A typical example is I ($1·7 \times 10^{-5}$ moles) in CCl_4 which before irradiation showed $\varepsilon \times 10^{-3}$ at 310, 410, and 640 mμ of 21·12, 2·00 and 17·02; after exposure the respective values were 17·49, 3·87 and 12·61. In all other cases there was also decrease in ε at the lowest and highest mμ and marked increase in the range of 410–440 mμ. These changes appear to be caused by partial rearrangement from the *trans* to the *cis* forms, although so far the latter has not been isolated. The polarity of these alkyl indigos is not great enough for the intramolecular attraction of negatively charged O and the positively charged N to stabilise the *trans* forms completely. In as much as irradiation of *N*-monoalkyl indigos caused no changes in absorption spectra, this *trans* form remains unchanged; this is also true for indigo itself. That partial reduction to indigo white (caused by $CHCl_3$) does not occur is shown by the fact that for tetramethyl indigo white ε in the critical 410–440 mμ region was practically zero. C.O.C.

Sensitising Dyes and other Cyanines

K. M. Hornsby

Brit. J. Phot., **104**, 270–272, 290–291 (1957)

Pyrylocyanines. I— Pyrylohemicyanines, Phenyl and Furyl Pyryl Polymethins

L. Roosens and R. Wizinger

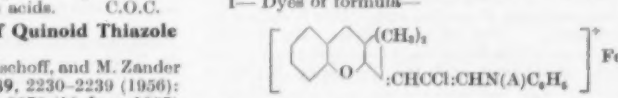
Bull. Soc. Chim., Belges, **66**, 109–124 (1957)

II— Condensation of the 1:2:3:4-tetrahydroxanthylium Nucleus with Aromatic and Heterocyclic Aldehydes

L. Roosens and S. Creyf

Ibid., 125–135; *Chem. Abs.*, **51**, 10530, 10531 (25 July 1957)

I— Dyes of formula—



(A = H or acyl) are obtained by condensing tetrahydroxanthylium tetrachloroferrate with $C_6H_5NHCH{:}CClCHO$ or similar aldehydes. Bromo analogues were also prepared, they have the same colours as the chloro compounds. The function of the chromophores and the convergence of the series are discussed.

II— Similar syntheses using aromatic and heterocyclic aldehydes are described. Aldehydes containing strong basic ring structures, e.g. pyridine 2- and 4-aldehyde would not condense even in strongly basic medium, presumably because of their poor susceptibility to nucleophilic attack. C.O.C.

Fluorescence Life Times of Photosynthetic Pigments
S. S. Brody
Univ. Microfilms (Ann Arbor, Mich. U.S.A.), *Publ.* No. **19802**, 94 pp.
(microfilm $2·00, paper enlargement $9·40)

Polarograms of Desensitising Dyes
S. Umano
Nippon Kagaku Zasshi, **77**, 796–801 (1956): *Chem. Abs.*, **51**, 7916 (10 June 1957)
The polarograms of C.I. Direct Red 28, Chrysoidine Extra, C.I. Basic Violet 14, C.I. Basic Violet 3, C.I. Basic Green 4, C.I. Basic Violet 1, C.I. Basic Red 5, C.I. Basic Red 2, Flavindulin, Pinakryptol Green, Acridine Red, C.I. Acid Red 94, Rhodamine Extra, C.I. Basic Blue 9 and Pinakryptol Yellow have been studied. From the half-wave potential, the electron affinities of the dyes were calculated and the results compared with electron-energy levels of Ag halides. It is possible that the photoelectrons of Ag halide crystal flow into the dyes adsorbed in the crystal surface. The electron affinity of dyes is roughly proportional to the degree of desensitisation. C.O.C.

Cyanine Dyes from the Isomeric Dimethylthiazolo-benzothiazoles
A. I. Kiprianov, A.V. Stetsenko and E. D. Seych
Ukrain. Khim. Zhur., **22**, 760–766 (1956): *Chem. Abs.*, **51**, 8725 (25 June 1957)
Preparation and properties of a considerable number of $R^1(CH{:}CH)_nCH{:}R^2$ iodides, e.g. 3-ethyl-6-methyl-2-benzo[1:2:4:5]bisthiazolyl-(CH:CH)-CH-3-ethyl-6-methyl-2-benzo[1:2:4:5]bisthiazolinylidene iodide, are described. C.O.C.

Cyanine Dyes from the Isomeric Pyridothiazoles
S. G. Fridman and A. I. Kiprianov
Ukrain. Khim. Zhur., **22**, 767–771 (1956): *Chem. Abs.*, **51**, 8725 (25 June 1957)
Formation and properties of dyes of type $R^1(CH{:}CH)_nCH{:}R^2{}_2X$, e.g. 1:4-dimethyl-2-thiazolo[5:4-*b*]pyridyl-(CH:CH)-CH:1:4-dimethyl-2(1*H*)-thiazolo[5:4-*b*]pyridylidene I_3, are described. The monoethyl *p*-toluenesulphonate of 2-methylthiazolo[4:5-*c*]pyridine does not give a cyanine dye and so the C_2H_5 is presumably on the pyridine and not the thiazole N atom. The bis(CH_3methosulphate)H_2O is dye forming. C.O.C.

Cyanine Dyes of the Naphthodithiazole Series
A. V. Stetsenko and V. I. Ivanova
Ukrain. Khim. Zhur., **22**, 772–775 (1956) *Chem. Abs.*, **51**, 8726 (25 June 1957)
An account of the preparation and properties of some $R^1(CH{:}CH)_nCH{:}R^2$ iodides, e.g. 3:7-dimethyl-2-naphtho[1:2:5:6]bisthiazolyl(CH:CH)CH:3-methyl-2-benzothiazolinylidene iodide. C.O.C.

Polymethin Dyes from Heterocyclic Pyruvic Acid Derivatives. I
W. Franke
Chem. Ber., **89**, 1887–1892 (1956): *Chem. Abs.*, **51**, 8073 (10 June 1957)
Syntheses of red dyes of the type—

$$QC(COCOOC_2H_5)CHCH{:}P$$

(Q = 2-benzoselenazolyl; P = 3-ethyl-2-benzothiazolinylidene), e.g. by refluxing the anil of P:CHCHO with $QCH_2COCOOC_2H_5$ in pyridine, are given. C.O.C.

Polymethin Dyes from Heterocyclic Pyruvic Acid Derivatives. II— Dyes from Heterocyclic-substituted Pyruvic Acid Oximes
W. Franke
Chem. Ber., **89**, 2727–2733 (1956): *Chem. Abs.*, **51**, 8728 (25 June 1957)
2-Benzothiazolepyruvic acid oxime when refluxed with 3-ethyl-2-(2-phenyliminoethylidene)-2:3-dihydrobenzoselenazole for 5 min. in acetic anhydride and pyridine yields the red—

$$o\text{-}\overline{C_6H_4\text{·}Se\text{-}C(:CHCH{:}C(2\text{-benzothiazolyl})CN)\text{·}NH}$$

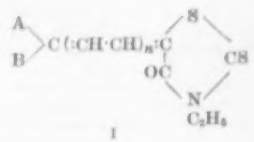
Other preparations of this type are described. C.O.C.

Synthesis of Azacyanines
H. Zenno
J. Soc. Sci. Phot. (Japan), **19**, 84–90 (1956): *Chem. Abs.*, **51**, 8757 (25 June 1957)
Condensation of monoximes of alloxans with reactive methyl groups of heterocyclic quaternary salts yields azamerocyanines. Thus violuric acid boiled with 2-picoline methiodide in alcohol or pyridine in presence of piperidine yields the reddish orange 1-methyl-2-[barbiturylidene-5-iminomethylene]-1:2-dihydropyridine. Use of monoximes of quinones or naphthoquinones in place of alloxanes yields azapolymethins. Condensation of alloxans or *p*-quinone with quaternary salts yields dyes of formula—

$$-N{:}C\text{·}CH{:}C\diagdown\!\!\diagup$$

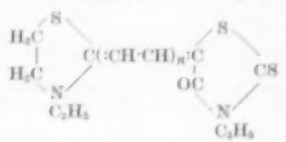
C.O.C.

Influence of Substituents on the Absorption of Neutrocyanines
H. von Rintelen and O. Riester
Mitt. Forschungslab. Agfa Leverkusen-München, **1**, 65–75 (1955): *Chem. Abs.*, **51**, 7913 (10 June 1957)
Neutrocyanines II of formula I—



I

(A = NR_2 or $\overline{N\text{·}(CH_2)_{m-1}\text{·}CH_3}$; B = SR) result from the interaction of quaternised (e.g. with methylsulphate) substituted dithiocarbamic esters (R_2NCSSR) with 3-ethylrhodanine or 3-ethyl-5-ethylidenerhodanine. Other neutrocyanines III (of formula I where A = B = NR_2 or $\overline{N(CH_2)_{m-1}\text{·}CH_3}$) result from the interaction of II with secondary amines, e.g. dimethylamine, pyrrolidine or piperidine. Compared with hemioxonols (IV) (I, where A = NR_2 or $\overline{N(CH_2)_{m-1}\text{·}CH_3}$; B = H, $n = 0$), dyes II ($n = 0$) absorb in benzene solution with λ max. at about 20 mμ longer wavelengths but with comparable intensities, while dyes III ($n = 0$) absorb very much like dyes IV ($n = 0$). Similar comparisons with dye I ($n = 1$) showed that dyes II ($n = 1$) again absorbed at somewhat longer wavelengths than the corresponding dyes IV ($n = 1$), but dyes III ($n = 1$) absorb at still longer wavelengths, the average bathochromic shift from a dye IV ($n = 1$) to a dye III ($n = 1$) being about 30 mμ. Comparisons are also made between dyes I and 5-(1:3-dimethyl-2(3*H*)-imidoazolylidene)-3-ethylrhodanine and thiazoline dyes of formula—



(n = 0 or 1). Syntheses of a large number of these dyes are described. C.O.C.

Dyeing Properties of *Glycyrrhiza glabra*
V. V. Ivanov and N. Korchebokova
Botan. Zhur., **41**, 1486–1488 (1956): *Chem. Abs.*, **51**, 8440 (10 June 1957)
An aqueous decoction of the roots dyes wool and silk directly from alkaline, neutral or acid baths, beige and light yellow respectively. It is a polygentic dye for both these fibres but has no affinity for cellulose. C.O.C.

The Colouring Matters of *Xanthoria fallax*. Fallacinal and Fallacinol
T. Murakami
Pharm. Bull. (Tokyo), **4**, 298–302 (1956): *Chem Abs.*, **51**, 8056 (10 June 1957)
Evidence proving that fallacinal is 2-formyl-4:5-dihydroxy-7-methoxyanthraquinone and fallacinol 2-hydroxymethyl-4:5-dihydroxy-7-methoxyanthraquinone. C.O.C.

Conditions of Production of "Red Iron Oxide" by Thermal Decomposition of various Iron Salts and Development of the Colour of the Pigments produced from them
L. N. Urpenskaya and A. Kh. Girenko
J. Appl. Chem., U.S.S.R. **29**, 1876–1879 (Dec. 1956)
The colour of the "Red Iron Oxide" pigment produced by the thermal decomposition of $FeSO_4$ is superior to the

colour of the pigments produced similarly from $Fe(NO_3)_3$, $Fe(NH_4)_2(SO_4)_2 6H_2O$, $Fe(OH)_2$, $Fe(OH)_3$, $FeCl_2$, $FeCl_3$, and $Fe(COO)_2$. T.Z.W.

The Colouring of Amethyst. II— Effect of Ultraviolet and γ-rays on the Colouring
J. Lietz and W. Münchberg
Neues Jahrb. Mineral., Monatsh., 25–33 (1957): *Chem. Abs.*, **51**, 10242 (25 July 1957)

Ultraviolet radiation destroys amethyst colour centres but does not affect the yellow to green produced by heating. The colour centres destroyed by ultraviolet irradiation or heating can be restored by γ- or X-rays. Amethyst colour centres thus produced can supplement the colours resulting from heating giving new colour tones. C.O.C.

Early Use of Lead Pigments and Cosmetics in China
E. H. Schafer
T'oung Pao (Leiden), **44**, 413–438 (1956): *Chem. Abs.*, **51**, 7779 (10 June 1957)

A history (in English) of the use of lead compounds as colorants in China. The oxides were in use in the 2nd millenium B.C. but white lead (C.I. Pigment White 1) was much more widely used as a cosmetic and for writing purposes but curiously was not much used in paints. C.O.C.

Pigments of old Russia
P. M. Lak'yanov
Priroda, **45**, (11), 77–82 (1956): *Chem. Abs.*, **51**, 8450 (10 June 1957)

The chemical properties, quality, and origin of pigments used in Russian artifacts during the 11th–16th centuries are discussed. C.O.C.

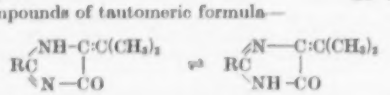
Pigments for Paint
G. Wormald
Paint, Varnish Production, **47** (4), 37–44 (5), 53–56 (6), 43–48 (1957): *Chem. Abs.*, **51**, 10088 (10 July 1957)

A comprehensive review of the composition, properties and uses of available blue, violet, orange, yellow, red, maroon and green pigments, 30 references. C.O.C.

PATENTS

Colour Couplers
Ilford *BP* 782,545

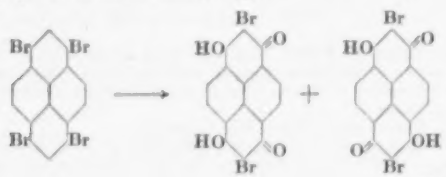
Compounds of tautomeric formula—



e.g. 2-phenyl-5-isopropylideneiminazol-4-one, yield magenta azomethin dyes when used as photographic colour couplers. These dyes have the advantage that they absorb almost entirely in the green region of the spectrum. C.O.C.

Preparation of Dibromo-di-Perinaphthindandion
General Aniline *BP* 781,257

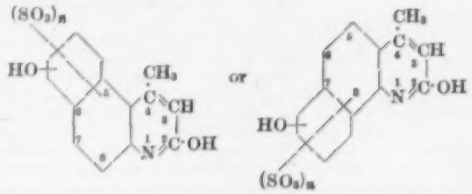
This intermediate for the production of naphthalene-1:4:5:8-tetracarboxylic acid is prepared by heating 3:5:8:10-tetrabromopyrene with 1–4% oleum at 145–160°c. Thus, 3:5:8:10-tetrabromopyrene (200) is added in 1 hr. to 100% H_2SO_4 (1530) and 20% oleum (270) at 25–30°c. The temperature is raised in 2 hr. to 150°c. and held for 3 hr. at 150–155°c. Evolution of SO_2, Br_2 and HBr occurs. The mixture is cooled and diluted with water (900) at 100–110°c. and the sulphate of di-bromo-di-perinaphthindandion crystallises at this temperature. The diluted melt is drowned into water (9000) and the product is filtered and washed. The 3:5:8:10-tetrabromopyrene is obtained by brominating pyrene in nitrobenzene at 120°c. The present process is an improvement on that of *USP* 2,009,596 in that the conditions are less corrosive whilst high yield is still attained (97%).



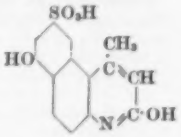
E.T.

Conversion of Aminonaphtholsulphonic Acids into Quinoline Derivatives— Coupling Components for Azo Dyes
Gy *BP* 782,062

N-Acetoacetyl aminonaphtholsulphonic acids are treated with dehydrating ring-closing agents (Knorr reaction) to give 2-hydroxy-4-methyl-5:6- or -7:8(hydroxybenzo)-quinolinesulphonic acids—



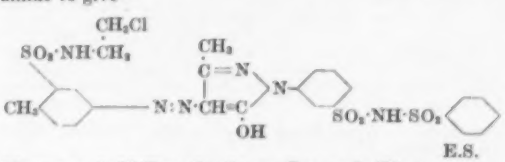
which are coupling components for direct dyes. Thus *N*-acetoacetyl-J acid is dissolved in 98% H_2SO_4 at room temperature, and stirred for 12 hr. at 30°c. Drowning out and purification by dissolving in aq. Na_2CO_3 and salting out gives a good yield of 2-hydroxy-4-methyl-5:6(3′-hydroxybenzo)quinoline-5′-sulphonic acid—



E.S.

Monoazo Acid Dyes
Ciba *BP* 779,818

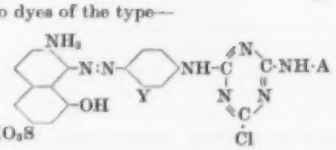
Monoazo compounds free of SO_3H groups but containing a monoacylated sulphonamide group and a sulphon-*N*-(haloalkyl)amide group dye wool, nylon, etc. from neutral or weakly acid baths. The yellows in which the sulphon-*N*-(haloalkyl)amide group is in the diazo component, and the coupling component is a pyrazolone, are particularly valuable. Thus 4-aminotoluene-2-sulphon-*N*-β-chloroethylamide is diazotised and coupled with 3-methyl-1-phenyl-5-pyrazolone-3′-sulphon-*N*-(benzenesulphonyl)-amide to give—



E.S.

Monoazo Acid Dyes having a Cyanuric Ring
Ciba *BP* 780,591

Monoazo dyes of the type—



(Y = SO_2Alk, SO_2Ar, SO_2Aralk, or preferably *N*-subst. sulphonamide group; A = Alk, Ar, cycloalk, or Aralk) give oranges, reds and violets on wool, nylon, etc. Thus *p*-phenylenediaminesulphon-*N*-ethyl-*N*-phenylamide is condensed with 1 mol. of 2-anilino-4:6-trichlorotriazine, and the product is diazotised and acid-coupled with γ-acid to give a red (Y = $SO_2{\cdot}N(C_2H_5)C_2H_5$; A = C_6H_5). E.S.

Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc.
Ciba *BP* 781,286

The 1:2 cobalt complexes of monoazo dyes of the type *o*-aminophenol → *o*-coupling naphthylamine, free of SO_3H or COOH groups, but containing a sulphone or preferably a sulphonamide group or groups, dye wool, nylon, etc. from neutral or weakly acid bath. Mixed complexes from 1 atom of Co, 1 mol. of this type of monoazo compound and 1 mol. of a monoazo compound *o*-aminophenol → acetoacetarylide are also claimed. Thus a mixture of the 2 monoazo

compounds 2-amino-6-nitrophenol-4-sulphonamide → β-naphthylamine and 2-aminophenol-4-sulphon-*N*-methylamide → acetoacet-*o*-chloroanilide is dissolved in aq. NaOH and stirred at 80–85°c. with $CoSO_4$. The Co complex formed dyes wool yellowish green. E.S.

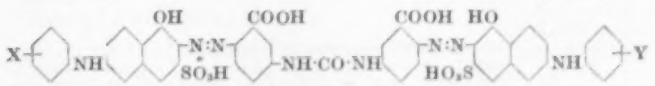
Metallisable Mono- and Dis-azo Disperse Dyes
ICI *BP* 780,509

Mono- and dis-azo disperse dyes, in which a heterocyclic compound containing the grouping—

(the N atom is part of a heterocyclic ring fused on to the benzene ring) is used as a coupling component, may be metallised, e.g. with Cu compounds, on cellulose acetate, nylon, or polyacrylonitrile fibres. Thus the monoazo dye *p*-nitroaniline → 8-hydroxyquinoline is applied to nylon at 85°c. from aq. dispersion, and the dyeing is then after-coppered at 95°c. in aq. $CuCl_2$, to give a red of good fastness to light and washing. E.S.

Copperable Disazo Direct Dyes
Ciba *BP* 781,484

Disazo dyes—



(either X or Y, or both, are water-solubilising groups such as SO_2NH_2, O·CH_2·COOH, COOH, or SO_3H) are more soluble and more level dyeing than the similar dyes in which X and Y = H, and give coppered dyeings little inferior in wet fastness. Thus J acid or 2:5-dihydroxynaphthalene-7-sulphonic acid is condensed with metanilamide in presence of a sulphite to give *N*-*m*-sulphamylphenyl-J acid, which is coupled with diazotised 4-nitroanthranilic acid. The nitro group is then reduced with NaSH, and 2 mol. of the aminoazo compound are condensed with 1 mol. of phosgene. The product (X and Y = *m*-SO_2·NH_2) dyes cotton and viscose red violet by the single or 2-bath after-coppering method. E.S.

Brown Trisazo Dyes for Leather
FH *BP* 779,486

Trisazo compounds—

amine→ [1-amino or 1-(*m* or *p*-aminobenzoyl) amino-8-naphtholmono(or di)sulphonic acid] →resorcinol←amine

(the amines are free of groups capable of metallisation, and at least one of them is an aminodiphenylaminesulphonic acid) dye leather brown of good resistance to alkalis, acids, and formaldehyde, and have good solubility. Thus H acid (monosodium salt) is diazotised and coupled with resorcinol. A suspension of 1 mol. of diazotised 4-amino-diphenylamine is then added, and aq. NaOH so that coupling takes place at pH 9. Finally 1 mol. of diazotised *p*-nitroaniline is coupled at pH 4. Salting-out yields the deep red-brown leather dye.

BP 779,487

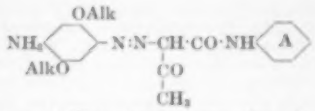
Similar results are given by trisazo dyes—

amine→ [1-amino or 1-(*m* or *p*-aminobenzoyl)-amino-8-naphtholmono(or di)sulphonic acid] →3:3′-dihydroxy-diphenyl ←amine

(at least one of the amines contains SO_3H). Thus diazotised H acid is coupled at pH 10 with 3:3′-dihydroxydiphenylamine. Diazotised sulphanilic acid is then added, and aq. NaOH. After adding sodium acetate a diazo soln. from 2-chloro-4-nitroaniline is added. The product dyes leather of various tannages dark red-brown. E.S.

Blue-green and Green Azoic Dyes and Disazo Pigments
FH *BP* 780,484

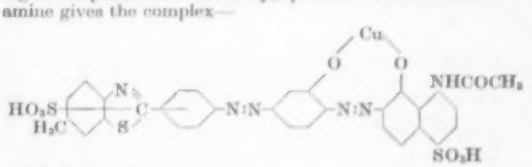
Aminomonoazo compounds—



(Alk = CH_3 or C_2H_5; the benzene ring A may have substituents other than SO_3H or COOH) are diazotised and coupled with arylides of 3:2-hydroxynaphthoic acid or of its 7-bromo or 7-alkoxy derivatives, in substance or on the fibre, to give blue-green and green pigments or azoic dyeings and prints. Thus diazotised 2:5-dimethoxy-4-nitroaniline is diazotised and coupled with acetoacetanilide, and the nitro group then reduced to an NH_2 group. The aminoazo compound so produced is diazotised, and the soln. so formed is used for developing a blue-green on cotton previously impregnated with an alkaline soln. of 3-hydroxy-2-naphthoanilide. E.S.

Metal(Copper and Nickel)-complex Disazo Direct Dyes Derived from Dehydrothio-*p*-toluidine
Ciba *BP* 781,086

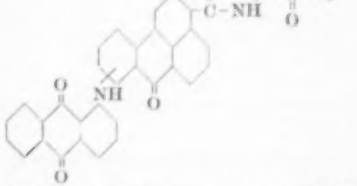
Disazo dyes of the type dehydrothio-*p*-toluidine → *o*-aminoalkoxy compound of benzene or naphthalene series → *N*-subst.-1-amino-8-naphtholmonosulphonic acid, are converted into Ni, or preferably Cu, complexes with splitting off of Alk from the OAlk group, to give direct dyes of good light fastness. Thus dehydrothio-*p*-toluidine is sulphonated with oleum and the sulphonic acid so produced is diazotised and coupled with *o*-anisidine-*m*-methanesulphonic acid. The monoazo compound so formed is hydrolysed at 90°c. with 4% aq. NaOH, and the aminoazo compound so formed diazotised and coupled with 1-acetylamino-8-naphthol-4-sulphonic acid, in presence of pyridine. Refluxing with aq. ammoniacal $CuSO_4$ in presence of monoethanolamine gives the complex—



which dyes cotton olive grey. E.S.

Benzanthrone Vat Dyes
FBy *BP* 779,508

Grey vat dyes are made by treating an anthraquinonylamino-bz-1-benzanthrone carboxylic acid-(α-anthraquinonyl)-amide—



with an alkaline condensing agent, e.g. alc. KOH at 100–200°c. The intermediate is prepared by the following stages:—(1) benzanthrone carboxylic acid is brominated in presence of iodine and chlorosulphonic acid (2) the product is converted to its acid chloride derivative by thionyl chloride in nitrobenzene (3) the acid chloride is condensed by adding an α-aminoanthraquinone to the melt and (4) this product is finally condensed with another molecule of an α-aminoanthraquinone in nitrobenzene with addition of Na_2CO_3 and Cu acetate. Further condensation of the grey vat dye under acid conditions e.g. with phosphoric acid at 200°c. results in its conversion to a green vat dye. E.T.

Acedianthrones
Ciba *BP* 779,542

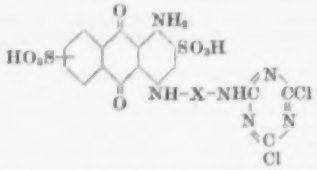
Acedianthrones, vat dyes or intermediates for vat dyes, are prepared from bis-(anthronylidene)-ethane which may

be either unsubstituted or substituted in one or both anthrone nuclei by Hal, –COOH or a functional derivative such as nitrile, Alk, Aryl, $-NO_2$, $-NH_2$, –NHOC·R, –OH or –OAlk. The intermediate is heated in an inert aliphatic halogen-containing solvent, e.g. tetrachloroethane, trichloroethylene etc., in presence of acetic, propionic or butyric anhydride and sulphuric acid (< 90%). The mixture is heated at 50–80°c. and finally at 80–120°c. to complete the reaction and the precipitated acedianthrone is separated by filtration. This method is better than the earlier process using $AlCl_3$, which normally gives resinous by-products, and than the method of *BP* 551,622 (*J.S.D.C.*, **59**, 155 (1943)). E.T.

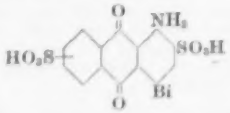
Water-soluble Anthraquinone Dyes for Cellulose

ICI *BP* 781,930

Blue-green to olive green dyes of formula—



(X = bridging group containing anionic solubilising group, e.g. $-C_6H_4C_6H_4-$ or $-C_6H_4N=NC_6H_4-$ containing $-SO_3H$ or –COOH) have good fastness to light and washing. They are produced in two stages—



is condensed with a diamine, e.g. *m*-phenylenediamine-4-sulphonic acid, 4:4′-diamino-azobenzene-2-sulphonic acid etc. in aq. alkaline medium. The product is then condensed with cyanuric chloride at 0–5°c. and separated by salting as its Na salt. The dyes may also be separated mixed with buffering agent, e.g. NaH_2PO_4 and Na_2HPO_4, to give pH 6·5 and are applied to cellulose by printing or dyeing. They are particularly suitable for dyeing by a continuous process. E.T.

Disperse Dyes containing Vinyl Sulphone Groups

FH *BP* 779,781

Cellulose acetate and polyamide fibres are dyed or printed with water-insoluble azo-, nitro- or anthraquinone-dyes containing the group—

$$-SO_2-CH=CH_2$$

These new dyes containing the vinylsulphone group are applied in the usual manner or they may be formed in the dyebath from dyes containing the groups—

$$-SO_2-CH_2-CH_2-OSO_2K$$

or $$-SO_2-CH_2-CH_2-Cl$$

by the action of weak alkali, e.g. soap solution or disodium phosphate. E.T.

Amino-benzophenone-sulphones—Yellow to Orange Disperse Dyes

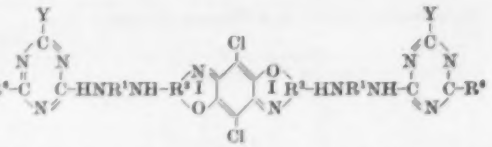
BASF *BP* 781,558

Amino-benzophenone-sulphones (amino-thioxanthone-*S*-dioxides) are yellow to orange disperse dyes giving dyeings with very good fastness properties. Benzophenone-sulphone (or its Hal, Alk, hydroxy or alkoxy derivative) is nitrated and the amino-derivatives are then obtained either by reduction or by replacement of the $-NO_2$ group by reacting with NH_3 or primary or secondary amines. Thus benzophenone-sulphone (4) is stirred for 8–10 hr. at room temperature with nitrating acid (70) containing HNO_3 and H_2SO_4 in the ratio of 51 to 49. The melt is diluted with water and the deposited nitro-compound filtered and washed neutral. This 1-nitrobenzophenone-sulphone (20) is heated with 50% aq. isopropylamine 5 hr. at 100°c. in a closed vessel. On cooling 1-*iso*propylamino-benzophenone-sulphone separates m.p. 190–191°c. E.T.

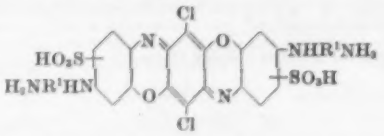
Oxazine Dyes

Ciba *BP* 781,384

Animal fibres synthetic super-polyamide and polyurethane fibres and cellulosic fibres are dyed with oxazine dyes of formula—



(R^1 = benzene residue; R^2 = benzene ring fused on to hetero ring I and containing $-SO_3H$ group; R^3 = res. of primary or secondary amine bound to the triazine ring and free from oxazine rings; Y = $-NH_2$ or Hal). The dyeings are of good purity and high light fastness. The dyes are made by condensing a cyanuric halide (2 mol.) with 1 mol. of a diamino-dioxazine, e.g.



which is itself produced by condensing 1 mol. 2:3:5:6-tetrachloroquinone (chloranil) with 2 mol. $H_2NR^2NHR^1NH$-Acyl (R^1 and R^2 = benzene residues with –NH– in *p*-positions and $-SO_3H$ in *o*-position to the $-NHR^1$) ring closing and splitting off the acyl groups. The cyanuric halide/diamino-dioxazine condensation product (1 mol.) is then condensed with 2 mol. of a mono-amine, e.g. amino-benzenes, amino-naphthalenes, aminodiphenyl compounds etc. Especially suitable are amino-monoazo dyes of formula—

$$H_2NR^3-N=N-R^4$$

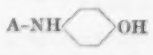
and $$H_2N-R^3-X-R^5-X-R^4$$

(R^3, R^4, R^5 = benzene residues; one X = azo link; other X = –CONH– group). E.T.

Sulphur Dyes

Gy *BP* 779,760

Blue or brown sulphur dyes are made by heating for 12 to 48 hr. under reflux a water-soluble organic solvent boiling above 100°c., an ethyleneglycol *mono*alkyl ether, an alkali polysulphide whose S content corresponds to a penta- to hepta-sulphide and a mixture of two *p*-hydroxy-phenyl arylamino compounds—



(A = phenyl, phenyl with a 4-substituted secondary or tertiary NH_2 group, *β*-naphthyl, *β*-anthracyl, 3′- or 6′-carbazolyl, Hal or Alk substitution product in one component; and A = a different radical selected from phenyl, alkylphenyl or halo-phenyl in the other component). The mixed sulphur dyes thus produced have improved wet and chlorine fastness and their dyeing properties are generally better than those of mixtures made from the same individually produced dyes. E.T.

Sulphur Dyes from Decacyclene

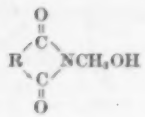
CFM *BP* 781,408

Yellow–brown khaki and black–brown sulphur dyes are made by treating polynitro-decacyclenes in chlorosulphonic acid with sulphur and Hal, simultaneously *or* consecutively, or with sulphur chloride. Thus, hexanitrodecacyclene (20) is stirred into chlorosulphonic acid (200); S (25) is added at 20–30°c. and, with temperature rising from 20 to 50°c., chlorine (20–25) is introduced. After 2–3 hr. at 50°c., the melt is poured on to ice and the dye separated by filtration. The product dyes cotton either from a vat or from a bath containing sodium sulphide. E.T.

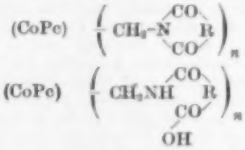
Phthalocyanine Vat Dyes

General Aniline *BP* 779,324

Blue vat dyes of excellent light fastness are made by reacting cobalt phthalocyanine with a 1:2-dicarboxylic acid (*N*-methylol) imide—



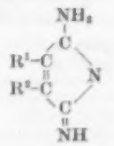
to give mixtures containing unchanged cobalt phthalocyanine and its acidylaminomethylated derivative. These mixtures are—



(CoPc = Co phthalocyanine; R = 1:2-divalent organic radical; n = 0·1 to 0·8). Dyeings are made from NaOH/hydrosulphite vats when the mixtures, particularly those where n = 0·4 to 0·6, give much superior results to Co phthalocyanine itself (n = 0) or the fully acidylaminomethylated derivative (n = 1). E.T.

Tetra-aza-porphin Dyes from 2-Amino-5-imino-pyrrolenine
FBy *BP* 781,499

Compounds of formula—



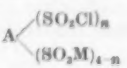
(R^1 = H, Alk, *cyclo*alkyl, aralkyl, Hal or phenyl; R^2 = Alk, *cyclo*alkyl, aralkyl or Hal), e.g. 3-methyl-4-ethyl-, 3-methyl-4-benzyl-, 3:4-dichloro-2-amino-5-imino-pyrrolenine, etc., a heavy metal or heavy metal compound and an organic solvent are heated to about 100°c. giving crystals of blue tetra-aza-porphin pigment dyes. Organic solvents with slight reducing properties are preferred, e.g. polyhydric alcohols or reducing acids, and the preferred metals are Ni, Cu and Co. Mixtures of the 2-amino-5-imino-pyrrolenines and a 1-amino-3-imino*iso*indolenine may also be used. These dyes may be formed on the fibre by applying the above reaction mixtures together with a thickening agent, printing on cotton or viscose, drying at 60°c. and subsequently developing by neutral or acid steaming or by dry heating at 120°c. These dyeings have outstanding fastness properties. E.T.

Phthalocyanine Vat Dyes
General Aniline *BP* 781,749

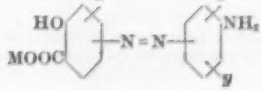
Vat dyes are produced by reacting Co phthalocyanine (1 mol.) with 0·1 to 5 equivalents of formaldehyde in presence of sulphuric, phosphoric or methylsulphuric acid (≤ 90% concentration) at 70–100°c. Preferably 0·3 to 1 equivalent of formaldehyde per mol. Co phthalocyanine is used and an amide is also added, e.g. acetamide, formamide, urea, etc. The products dye full clear blue shades of excellent light fastness. E.T.

Water-soluble Mordant Azophthalocyanine Dyes
DH *BP* 779,489

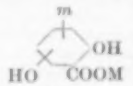
Phthalocyanine sulphochlorides of formula—



(A = subst. or unsubst. metal phthalocyanine res. derived from phthalimides having $-SO_2Cl$ and $-SO_2M$ in 3- or 4-positions; M = H, NH_4 or alk. metal; n = 2 to 4) are condensed in aq. medium in presence of an acid binding material with (1) 1–3 mol. of one or more amino-azo dyes of formula—



(x = H, Hal, CH_3, OH, NO_2 or SO_3M; y = H, Hal, Alk, alkoxy, NO_2, SO_3M or COOM; z = H, Hal, Alk, alkoxy; $-NH_2$ group is *m*- or *p*- to azo linkage) and (2) 1–3 mol. of a dihydroxybenzene carboxylic acid—

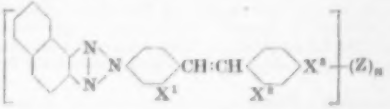


(m = H, Hal, OH, CH_3 or SO_3M)

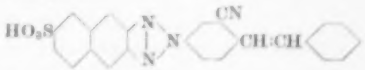
The above reactions may be carried out step-wise or simultaneously and any unreacted $-SO_2Cl$ group is hydrolysed in the final product. The resulting water-soluble mordant dyes yield purer dyeings and have superior fastness properties than the mordant dyes claimed in *BP* 768,444 (J.S.D.C., **73**, 275 (June 1957)) and *BP* 763,343 (J.S.D.C., **73**, 111 (March 1957)). E.T.

Monotriazole Fluorescent Brightening Agents
Gy *BP* 781,821

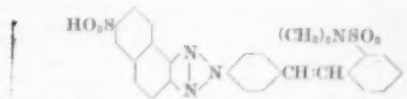
Compounds of formula—



(the aromatic rings may be further substituted except with chromophoric or auxochromic groups nor must the stilbene radical contain an azole ring or an acylamino or triazinylamino groups; there must be at least one electrophoric substituent in one of the X positions except that X^1 must not be a sulphonic acid group; Z = an acid salt forming group; n = 1–4) are fluorescent brightening agents having affinity for cellulose, polyamide and polyurethane fibres. Thus the compound—



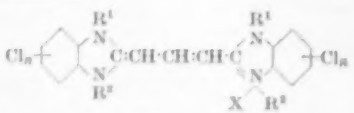
is useful for application to cellulose, soaps and synthetic detergents, while



is used on nylon. C.O.C.

Symmetrical Carbocyanine Dyes
Eastman Kodak Co. *USP* 2,739,149

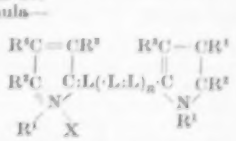
Dyes of formula—



(R^1 = Alk or Ar; R^2 = Alk; X = anion; n = 1 or 2) are produced by condensing a suitable quaternary salt with diethoxymethyl acetate or chloral alcoholate. Thus 5-chloro-1:3-diethyl-2-methylbenzimidazolium iodide condensed with chloral alcoholate yields the orange to red dye 5·5′-dichloro-1:1′:3:3′-tetraethylbenzimidazolocarbocyanine iodide. They sensitise silver halide emulsions to the blue-green region of the spectrum but not to the red region. C.O.C.

Cyanine Dyes containing a 3:5-Diarylpyrrole Nucleus
Eastman Kodak Co. *USP* 2,739,148

Dyes of formula—



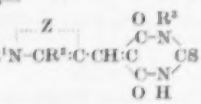
(R^1 = Alk or *cyclo*alkyl; R^2 and R^3 each = Ar; R^4 = H; Alk or Ar; L = subst. or unsubst. methin; n = 0, 1 or 2,

X = anion) are obtained by condensing suitable pyrrole bases with formic acid, formaldehyde, a diarylformamidine, a trialkyl ortho carboxylate, benzotrichloride, monocarboxylic acid halides, benzoyl chloride, etc. Thus bis-2-(1-methyl-3:5-diphenylpyrrolo)trimethin cyanine perchlorate is obtained by treating 1-methyl-2:4-diphenylpyrrole in warm alcohol with β-ethoxyacraldehyde diethylacetal and aqueous perchloric acid. It is a green-blue dye which is photographically inert but readily bleached by alkaline photographic developing solutions. C.O.C.

Monomethin Dyes containing a Thiobarbituric Acid Nucleus

Eastman Kodak Co. *USP* 2,739,147

Dyes of formula—

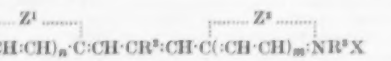


(R¹, R² and R³ = Alk or Ar; Z = atoms to complete a pyrrole ring), are obtained by condensing a suitable aldehyde with a thiobarbituric acid, e.g. 5-[(1-*cyclo*hexyl-2:5-dimethyl-3-pyrryl)-methylene]-1-phenyl-2-thiobarbituric acid is obtained from 1-phenyl-2-thiobarbituric acid and 1-*cyclo*hexyl-2:5-dimethylpyrrole-3-aldehyde. C.O.C.

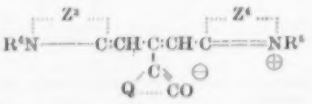
Carbocyanine Dyes

Kodak *BP* 783,329

A dye of formula—



(R¹ and R² = subst. or unsubst. Alk; R³ = subst. or unsubst. thienyl group; X = anion; Z¹ and Z² = atoms to complete 5- or 6-membered rings; *m* and *n* each = 0 or 1) and one of formula—

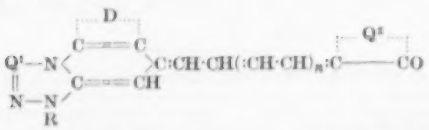


(R⁴ and R⁵ = Alk; Q = atoms to complete a 5- or 6-membered heterocyclic ring; Z³ = atoms to complete a benzothiazole, naphthothiazole, benzoselenazole, naphthoselenazole or naphthoxazole nucleus; Z⁴ = atoms to complete a naphthothiazole or naphthoselenazole nucleus) are used as a photographic supersensitiser, e.g. a mixture of 3:3′-dimethyl-9-(2-thienyl)-4:5:4′:5′-dibenzothiocarbocyanine *p*-toluene sulphonate and 5-[di(1-ethyl-2-β-naphthothiazolylidene)*iso*propylidene]-1:3-di(β-methoxyethyl)barbituric acid. C.O.C.

***mero*Cyanine Dyes**

Kodak *BP* 782,311

Dyes of formula—

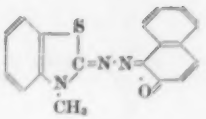


(R = Alk or aralkyl; D = atoms to complete a subst. or unsubst. benzene ring; *n* = 0 or 1; Q¹ = N or methin; Q² = atoms to complete a 5- or 6-membered heterocyclic ring), e.g. 3-ethyl-5-[(3-ethyl-5-*s*-triazolo[4:3-*a*]-quinolylidene)ethylidene]rhodanine, have photographic sensitising properties. C.O.C.

Azo or Diazacyanine Dyes by Condensation of Heterocyclic Hydrazones with Coupling Components

BASF *BP* 782,310

Hydrazones of *N*-alkyl(or phenyl)benzthiazolone (2) and similar 5- or 6-membered heterocyclic compounds are condensed under mild oxidising conditions with coupling components— phenols, naphthols, keto–enol compounds— to give azo or diazacyanine dyes. Thus *N*-methylbenzthiazolone-(2)-hydrazone and β-naphthol dissolved in aq. methanol are treated with ammoniacal potassium ferricyanide. The product is assigned the formula—



E.S.

Carotenoids from *Bixa orellana* (C.I. Natural Orange 4)

M. A. Moriez-Smith *BP* 781,809

The whole of the carotenoid and wax pigment content of the pulp of the dry, ripe seeds of *Bixa orellana* is soluble in hot polar organic liquids but only part is soluble in non-polar organic liquids, while a further portion is insoluble both in non-polar and cold polar organic liquids. This enables all the carotenoid and wax pigments to be not only extracted from the seed pulp but to be separated quantitatively into *cis*-bixin, *trans*-bixin and an oleoresinous fraction useful for colouring foods and medicinal preparations. C.O.C.

Calcination of Alumina Hydrate

Dorr-Oliver Inc. *BP* 781,994

An improved method using the fluidised-bed technique. C.O.C.

Silicate Pigments

J. M. Huber Corpn. *USP* 2,739,073

White pigments chemically analogous to zeolites and having very fine particle size and unusual brightness are produced by reacting together very dilute solutions of an alkali silicate and an aluminium salt. C.O.C.

Berlin Blue (C.I. Pigment Blue 27)

Chemische Fabrik Wesseling *BP* 782,076

Addition of lacquer constituents, especially plasticisers, to the mixture of ferrous salt solution and K or Na ferrocyanide, i.e. during the formation of the "Berlin White", results in an extraordinarily finely divided precipitate. This precipitate shows no tendency to agglomerate as the coating has already been formed on the particles of ferro-ferrocyanide. The coating does not interfere with the oxidation to the finished pigment which remains as a loose powder even after drying. The components of this coating are readily taken up by a lacquer into which the pigment is introduced. C.O.C.

Colour Reactions of Vat Dyes, Mainly of Polycondensed Systems and Their Derivatives in Sulphuric Acid. I— Basicity of the Carbonyl Group of Polycondensed Aromatic Amines in Sulphuric Acid (XIV p. 532)

V— PAINTS; ENAMELS; INKS

Single-coat Multicolour Finishes

A. Tremain and W. Morris

Paint Technol., **21**, 83–87 (1957): *Chem. Abs.*, **51**, 10090 (10 July 1957)

Multicolour finishes are aqueous suspensions of pigment paint or lacquer particles. The aqueous phase is usually clear and colourless while the paint phase generally consists of 3 or 4 colours. They can be made by stirring cellulose nitrate lacquers into an aqueous solution of methylcellulose containing a stabilising agent. C.O.C.

Dispersion of Pigments in Lipstick

M. Jakovics

Soap, Perfumery & Cosmetics, **30**, 398–400 (1957)

PATENTS

Coating Composition containing Copper Bronze Flake

DuP *BP* 781,826

Compositions which do not gel during storage, resist early tarnishing and/or dulling during prolonged outdoor exposure and have good crazing resistance are obtained by using polymerised methyl methacrylate of mol. wt. 55,000–105,000 as the vehicle for copper bronze flake pigments (C.I. Pigment Metal 2). C.O.C.

Paints

Tri Foods Co. *USP* 2,739,072

A paint vehicle consists of an emulsion of a drying oil in fermented whey having a lactic acid content of 1–2%. C.O.C.

Solid Solvent-type Artists' Paints
M. M. Januszewski *BP* 782,576
A solid-film forming base is formed into a gel by addition of a volatile solvent, pigmented and then the solvent removed. The resulting solid product can be applied by use of a brush impregnated with a solvent for the film-forming base. C.O.C.

Printing Inks
National Lead Co. *USP* 2,739,067
A clay having base exchange properties is reacted with an onium compound and then used as a stabiliser for suspensions of an ink base in a vehicle. C.O.C.

Erasable Inks
Venus Pen and Pencil Corpn. *BP* 781,808
A dispersion of fine crystalline flake graphite (C.I. Pigment Black 10) in a non-hardening non-polar solvent, when used in ball point pens yields writing which is erased as readily as that produced by lead pencils. C.O.C.

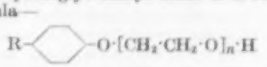
Inks for Carbon Papers
Columbia Ribbon & Carbon Manufacturing Co. *BP* 780,492
Vinyl polymers, especially soft vinyl chloride–acetate copolymers, are excellent bases for inks for carbon papers. Their use enables a thicker layer of ink to be applied than hitherto without any tendency to become mushy or cause hollow centres in the carbon paper. C.O.C.

VI— FIBRES; YARNS; FABRICS

Study of Sulphate in Cellulose Nitrate using $^{35}SO_4^{2-}$ as Tracer
A. G. Bricknell, L. W. Trevoy, and J. W. T. Spinks
Canadian J. Chem., **35**, 704–714 (July 1957)
When samples of cellulose nitrate, both stabilised and unstabilised and containing varying proportions of residual SO_4^{2-}, were immersed for periods up to 48 hr. in dil. $H_2{}^{35}SO_4$, there was no significant exchange of $^{35}SO_4^{2-}$ from the soln. with SO_4^{2-} from the fibres. Thus, the sulphate ions in cellulose nitrate are not simply adsorbed on the surface. It is suggested that they are occluded within the fibre structure. This sulphate may be removed by continued stabilisation (boiling in H_2O for 48 hr.), but only at the expense of fibre degradation. A.J.

High-bulk and Crimped Yarns
Anon.
S.V.F. Fachorgan, **12**, 361–362 (May 1957)
List of 62 references. C.J.W.H.

Technology of the Polyacrylonitrile Fibre Nitron (Nitrolon)
E. S. Roskin
J. Appl. Chem. U.S.S.R., **30**, 124–130 (Jan. 1957)
A good-quality Nitron fibre was produced on a pilot-plant scale by extruding the acrylonitrile polymer (mol. wt. 25,000–50,000) into a coagulating bath consisting of castor oil, carbon tetrachloride, butyl alcohol with polyethyleneglycol alkyl ether, a mixture of dimethylformamide, water, and the ether, and finally the ether alone. Polyethyleneglycolalkyl ether is a compound of a general formula—



where R is an alkyl group containing 8–12 C. T.Z.W.

PATENTS

Amine Modified Viscose Rayon
Vereinigte Glanzstoff-Fabriken *BP* 779,805
An improved process for spinning amine-modified viscose yarns is described in which an amine complex (0·06–0·4%) of formula $[MeX_4]An$ is added to the viscose with a gamma value > 42.
[Me = Fe, Zn, Cr, Cd or Sn
X = alkyl amine, alkanolamine or aryl amine
An = Cl, SO_4 or NO_3].
e.g. $[Fe((C_2H_4OH)_2N)_6]Cl_3$.
W.G.C.

Casein Fibres
Courtaulds *BP* 779,502
The water imbibition of protein fibres can be reduced by adding a polymer having amide side chains, e.g. polyacrylamide, to the spinning solution and treating the regenerated fibres with formaldehyde. W.G.C.

Polyvinyl Alcohol Fibres
FH *BP* 779,815
Polyvinyl alcohol fibres are hardened by incorporating in the spinning solution a linear polymer with reactive hydrogen at an amide nitrogen, and heating the spun fibre with a reactive carbonyl compound in presence of an acid catalyst. The carbonyl compound is usually formaldehyde and a wide range of linear polymers may be used, e.g. acrylamide gives a fibre with acid dyeing properties. W.G.C.

Acrylic Fibres having Improved Dyeing Properties
Courtaulds *BP* 780,857
The dyeing affinity of acrylic fibres is improved by treating the freshly spun fibres before drying with caustic soda or caustic potash. W.G.C.

Acrylic Fibres having a Scaly Surface
Dow Chemical Co. *BP* 780,375
Delustred fibres having a minute scale-like surface pattern resembling wool are produced by stretching the fibres, following or during abrupt coagulation, to rupture the surface sheath. W.G.C.

Modification of Linear Polymers by the Addition of Microgels
DuP *BP* 781,185
The properties of fibre-forming linear polymers can be modified by incorporating in the spinning solution, a microsol made from a microgel and a liquid common to or miscible with the solvent of the solution. Examples are given of acrylic, cellulose and polyurethane fibres modified with microgels of cross-linked acrylic polymers. W.G.C.

Polyester Fibres having High Affinity for Disperse Dyes
ICI *BP* 777,574
The fibres formed from a mixture (formed by melt blending) of a polyester formed by heating a glycol of formula $HO(CH_2)_nOH$ ($n = 2$–10) with terephthalic acid with a polyester formed by heating a glycol of formula $HO{\cdot}CH_2{\cdot}CH_2{\cdot}(O{\cdot}CH_2{\cdot}CH_2)_n{\cdot}OH$ ($n = 1$–5) with terephthalic or *iso*phthalic acid, when treated with an *N*-aryl-arylamine, e.g. *NN'*-di-β-naphthyl-*p*-phenylenediamine have high affinity for disperse dyes and good resistance to degradation in air or oxygen. C.O.C.

Effects of Mercerisation on the Lateral Order Distribution of Cellulose (X p. 529)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Bleaching Hair for Dyeing
A. Gómez
Monit. Farm. y Terap. (Madrid), **63**, 105–106 (1957): *Chem. Abs.*, **51**, 10845 (25 July 1957)
Hair for dyeing is bleached with a mixture of 3% H_2O_2 (97 parts), wetting agent (ethyl sulphate of alkylethylmorpholine) (1·5), tartaric, citric, adipic or preferably glutamic acid (0·9) and Na_2SnO_3 (0·6). C.O.C.

PATENT

Iron-catalysed Decomposition of Sodium Chlorite
U.S. Secretary of Commerce *USP* 2,739,032
Addition of $\geq$ 0·04% of an iron salt to a solution of sodium chlorite increases the rate of decomposition. This rate can be subsequently decreased by addition of a non-ferrous oxalate, tartrate or citrate. C.O.C.

VIII— DYEING

New Developments with the Pad-Roll Method
B. F. Mellbin
Tex., **15**, 1729–1737 (Dec. 1956): *Textil Praxis*, **12**, 370–377 (April 1957)

Affinity of Acid Dyes
F. I. Sadov and I. A. Shikanova
Tekstil prom., **17**, 39–41 (April 1957)
The thermodynamic derivation of the affinity of polybasic acid dyes for protein fibres and 6-nylon based on the method of pH measurements when the fibre is half-saturated with dye is recommended. G.J.K.

Dyeing of Wool with Vat Dyes

N. G. Klemin and P. V. Morŷganov

Tekstil. prom., **17**, 35–39 (April 1957)

Vat dyes are successfully applied to wool from a weakly alkaline vat using triethanolamine instead of caustic soda. This facilitates dye dissolution and brings about quick reduction of the dye by Rongalite and admixed sodium hydrosulphite, dyeing being carried out for 30 min. only at 50–65°c. (pH 9·5–10·5; liquor ratio 1:50). The degrading effect of triethanolamine, sodium hydrosulphite and soda on the wool fibre, which is additive, is found to be less, under otherwise identical conditions, in the presence of the dye (2–4 g./litre). The degrading effect of the dye on the fibre is structure dependent, being least for Algol Red ZbZh. Tendering of wool is not greater than in the case of acid or mordant dyes. G.J.K.

Azoic Dyeing of Amilan (6-Nylon). I— Absorption of Azoic Coupling Components and Azoic Diazo Components under Various Conditions

T. Yonehara and S. Umekage

Toko Rayon Shuko, **10**, 1724 (1955)

II— Absorption of C.I. Azoic Coupling Component 2 and Diazo Components from the Same Bath and Developing the Dye

Ibid., 63–68

I— Amilan cannot be dyed by the conventional azoic technique but can be dyed by impregnating with the azoic coupling component and azoic diazo component from the same bath and then developing at a higher temperature. The amount of each component absorbed under various conditions has been ascertained.

II— The amounts of C.I. Azoic Coupling Component 2 and various azoic diazo components absorbed from the same bath has been investigated to find out the optimum conditions for the one bath dyeing of Amilan. C.O.C.

Dyeing of High-bulk Orlon

H. Stern

S.V.F. Fachorgan, **12**, 336–339 (May 1957)

The dyeing of high-bulk Orlon with disperse (Cibacet) and modified basic (Deorlene) dyes is described together with details of their fastness properties. Special attention is given to the treatment of knitted garments, which are dried after dyeing either by wet or dry tumbling. B.K.

Investigation of the Secondary Structure of Anodic Surface Layers of Aluminium by Dye Adsorption. II— Kinetics of Dyeing

T. Skulidis, C. Papathanasiu, and J. Marangosis

Kolloid-Z., **150**, 54–60 (1957):

Chem. Abs., **51**, 10207 (25 July 1957)

The amount of dye adsorbed X by either of the two Al_2O_3 layers in time t is given by the equation, $X^2 = kt$; this indicates a chemical reaction. The energy of activation is 21·5 k.cal./mole, corresponding to control of rate by interchange of places between dye and Al_2O_3, rather than by diffusion. In the first or X_1 layer, the rate constant k is proportional to the amount of electric charge that has been passed, whereas as for the second or X_2 layer it is independent of the amount of charge. C.O.C.

PATENTS

Dyeing Textiles with Inorganic Metallic Compounds

Crosland & Pickstone *BP* 778,415

Heating dry cellulosic material which has been dyed with mineral khaki, iron buff or the like to > 120°c. for a few minutes deepens and reddens the colour depending upon the time of heating and the temperature. The greater the proportion of iron salts used in producing the dyeing the greater the colour change. C.O.C.

Continuous Vat Dyeing of Vegetable Fibres

Standfast Dyers & Printers *BP* 778,945

Use of a vat containing 120–400 g./l. of caustic alkali leads to great saving in dye, thus use of 200 g./l. leads to a 50% reduction in the consumption of some dyes, the depth of the dyeing being the same as that obtained from a conventional vat. A list of suitable dyes is given. C.O.C.

Dyeing with Metal-complex Dyes

BASF *BP* 777,389

Dyeings of very good fastness to rubbing are obtained on wool with metal complex dyes if the wool is treated before, after, or during dyeing with water-soluble salts of acid polybasic acid esters whose ester group is derived from a reaction product of 20 mol. ethylene or propylene oxide and 1 mol. hydroxy-alkylatable compound of 5 C, e.g. Na salt of the acid sulphuric acid ester of the addition product of 80 mol. ethylene oxide to 1 mol. oleyl alcohol. C.O.C.

Dyeing or Printing Polyester Fibres with Metallisable Dyes

ICI *BP* 777,377

Terylene or the like can be satisfactorily dyed or printed with metallisable dyes if a co-ordination compound of a metal is used as the metallising agent either before or after dyeing. Thus Terylene is dyed with an aqueous dispersion of 4-anilino-5-nitro-chrysazin at 130°c. and then treated at 130°c. with an aqueous dispersion of the Cu complex of acetylacetone to yield a greenish blue fast to light, washing and dry heat. C.O.C.

Dyeing Polyacrylonitrile Fibres

Kunstzijdespinnerij Nyma *BP* 777,534

Copolymers of acrylonitrile having little or no affinity for normal acid dyes from an aqueous bath are readily dyed from an aqueous bath at > 100°c. containing a metal-dye complex and a water-soluble alkali metal salt. C.O.C.

Dyeing properties of *Glycyrrhiza glabra* (IV p. 521)
Tetra-aza-porphin Dyes from 2-amino-5-iminopyrrolenine (IV p. 525)
Printing and Pad-dyeing (IX below)

IX— PRINTING

Use of *p*-Aminoazobenzene in Aniline Black Printing

G. Aronovici

Ind. textilă (Bucharest), **12**, 555–558 (1956):

Chem. Abs., **51**, 9164 (25 June 1957)

Addition of *p*-aminoazobenzene to the printing paste prevents tendering of the fibre, as it neutralises any mineral acid liberated during ageing. The oxidation products of the *p*-aminoazobenzene also help to give more deeply coloured prints. C.O.C.

Accuracy of Colour Reproduction of Colour Films

W. Grossmann

Farbe, **5**, 23–40 (Sept. 1956)

PATENTS

White Discharges on Vat Dyeings

BASF *BP* 776,721

Vat dyes, including those hitherto regarded as difficult or impossible to discharge, can be discharged to white by use of a paste which contains in addition to the reducing agent and other additions a water-soluble polymer of *N*-vinyl pyrrolidines or their water-soluble copolymers with other vinyl compounds, preferably those of K value about 60. C.O.C.

Discharges on Dyeings of Disperse Dyes

Hardman & Holden *BP* 777,392

Excellent discharge of very great sharpness are obtained by (1) Mechanically impregnating polyester, cellulose triacetate, polyacrylonitrile and the like fibres with a dischargeable, disperse dye and then mildly drying, (2) Printing with a paste containing formamidinesulphinic acid, (3) Steaming with saturated steam at atmospheric pressure, (4) Heating the cloth in a continuous process at 150–170°c. with use of pressure, (5) Soaping at the boil, rinsing and drying. C.O.C.

Preparing Azoic Printing Pastes

FBy *BP* 778,928

Diazamino compounds formed from diazotised halogen-substituted aniline or halogen-substituted alkyl- or alkoxy anilines and 2-alkylamino-5(4)-sulphobenzoic acids when used in printing pastes together with azoic coupling components and caustic alkali on development with neutral steam in absence of a volatile organic base yield very deep and strong prints on cellulosic fibres and of good fixation on spun rayon. C.O.C.

Colour Correction in Multilayer Material for Colour Photography

Agfa AG für Photofabrikation *BP* 782,173

Printing and Pad-dyeing

S *BP* 776,796

An aqueous viscose solution containing a pigment and urea, thiourea, urethane, a water-soluble thiocyanate or a

polymethylene amine is applied, and the dyeing or print treated to regenerate cellulose from the viscose. C.O.C.

Transfers for Ceramics
Johnson, Matthey & Co. *BP* 778,453

A layer of varnish is applied to the transfer paper in the area it is desired to colour and then the desired colour is dusted on while at the same time a hardening catalyst for the varnish is also applied. The varnish is then hardened and any colour on the non-varnished areas removed. This process is repeated until the desired multi-coloured pattern is formed. This prevents hardening of the varnish before the colour is applied and also prevents staining of one colour by another. C.O.C.

Fast-to-light Colour-developed Multicolour Prints
Agfa AG für Photofabrikation *BP* 779,223

The fastness to light of colour-developed multicolour prints are much improved if the layers for the partial colour images are arranged, starting from the base in the sequence yellow, magenta and blue-green and if the prints are treated with a substance absorbing ultraviolet radiation together with an aliphatic aldehyde, e.g. a fluorescent brightening agent and formaldehyde. C.O.C.

Pressure-sensitive Recording Material
Malineus & Co. *BP* 778,353

A pressure-sensitive recording material taking a coloured impression without use of an external colouring agent is obtained by application of a thin coherent layer of lacquer such as cellulose nitrate or other film forming substance, over the pressure-sensitive side of the recording material. An example of a suitable lacquer is nitrocellulose (10 parts by weight), acetone (25), ethyl alcohol (70), water (3), glycerine (2), butyl stearate (8). G.S.B.

Dyeing or Printing Polyester Fibres with Metallisable Dyes (VIII p. 528)
Inlay Effects on Embossed Fabrics (X this page)

X—SIZING AND FINISHING

Effects of Mercerisation on the Lateral Order Distribution of Cellulose
Y. Tsuda and S. Mukoyama
Bull. Chem. Soc. Japan, **30**, 271–273 (April 1957)

Mercerisation of cotton linters and of sulphite and sulphate wood pulps causes a broadening of the lateral-order distribution curve and all three celluloses show almost the same distribution after mercerisation. For cotton linters the change in distribution is most marked by treatment with NaOH soln. of concn. 13–15% at 20°c., coinciding with the concn. required for the phase transition from cellulose I to cellulose II. A.J.

Finishing of Knitted Goods of High-bulk Terylene
G. McLeavy
S.V.F. Fachorgan, **12**, 346–348 (May 1957)

Processing is described under the following headings—relaxation or shrinking to develop maximum bulk; heat fixation usually in bulk form; dyeing by standard methods; light pressing at elevated temperature together with steam. B.K.

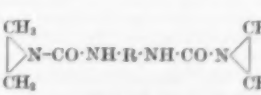
PATENTS

Tinting a Web of Textile Fibres
T.M.M. (Research) *BP* 779,905

A web of textile fibres, before carding, is passed over a transfer roller which dips into the colouring solution, e.g. a fugitive dye. W.G.C.

Coating Fibrous Materials, particularly Glass Yarn, with Synthetic Resin
Institut Textile de France *BP* 781,489

A permanent coating resistant to immersion in water and mechanical stress is obtained by first applying a compound of formula—



(R = aliphatic or aromatic), e.g. the product obtained by reacting 1 mol. of tolylene di*iso*cyanate with 2 mol. ethylene imine. This is followed by application of a mixture of the above compound, an organic di*iso*cyanate and the synthetic resin. Finally the treated yarn is heated, e.g. by drying at 150°c. for 15 min. C.O.C.

Rendering Cotton Resistant to Water and Chemicals
Commonwealth Engineering Co. of Ohio *BP* 777,877

The cotton is impregnated with a solution of dextran, then treated with an alkaline solution of an alkylating agent and finally heated to > 100°c. to complete the alkylation of the dextran. The treated fibres are unaffected by water, alkalis, mineral acids and the lower aliphatic alcohols but become tacky when treated with acetone, dioxane, benzene or toluene. C.O.C.

Compressive Shrinking of Fabrics
R. R. Walton *USP* 2,765,513–4

Apparatus in which the fabric is fed more quickly into the zone where the compression is to be applied than it is taken out, the distance between it entering and leaving the zone being extremely small. This ensures that compression is exerted warpways only and avoids any tendency of the fabric to buckle or form pleats. C.O.C.

Raising the Safe Ironing Point of Cellulose Triacetate
BrC *BP* 776,346

The safe ironing point of cellulose triacetate is raised by treating it with an organic swelling agent and so increasing its crystallinity. Thus cellulose triacetate fabric of safe ironing point 170°c. when treated for 10 min. in 50% aq. acetone at 20°c. had its safe ironing temperature raised to 200°c. while 20 min. treatment raised it to 210°c. C.O.C.

Elastic Yarns and Fabrics
Bleachers' Assocn. and Bradford Dyers' Assocn. *BP* 777,449

Yarn or fabric formed from synthetic thermoplastic fibres is mechanically shrunk to less than its natural length, heat set and allowed to cool. The treated yarn or fabric extends readily under low tension and recovers to its shrunk length when the tension is released. Suitable machinery is described. C.O.C.

Stretchable Fabrics
Grove Silk Co. *BP* 781,030

Yarn of stretched micro-crystalline polymer pre-set, then twisted and the twist set by a treatment which is less rigorous than the pre-setting. The twist is then removed so that the yarn becomes dead and non-lively while retaining potential twist, after which it is made into fabric. The fabric is then treated so that some of the potential twist is released, e.g. by immersion in boiling water. C.O.C.

Water-repellent Finish
FH *BP* 777,466

A good hydrophobic effect and excellent pearling off is obtained by treating the material with an organic solvent solution of a mixed salt of Al containing for each gram-atom of Al 1·5–2·8 gram-ions of the acid radical of an organic monobasic acid which boils or sublimes at 200°c. together with 0·2–1·5 gram-ions of the acid radical of a sparingly volatile organic acid compound of high mol. wt. capable of forming salts with Al. The total acid radicals should be 3·0 gram-ions per gram-atom of Al. Thus dry cleaned cotton or wool garments are treated for 15 min. at 20°c. with a solution of Al acetate stearate, paraffin wax and paraffin slack wax in CCl_4 or benzine and then dried at 70°c. This imparts a very good water repellent effect. C.O.C.

Water-repellent Finish
FH *BP* 780,967

An organic solvent solution of a solid or semi-solid paraffin hydrocarbon, a wax or thick oily to solid polychlorinated hydrocarbon, a carboxylic or sulphinic acid and a Zr and/or Al alcoholate is used. Thus wool gaberdine is impregnated for 10 min. at 20°c., using a liquor ratio of 1:20, with a solution in perchloroethylene of the condensate of Zr *iso*propylate with stearic and acetic acids. It is then squeezed off until it contains its own weight of liquor and dried at 120°c. This gives an excellent water-repellent finish having remarkable flame-resistant properties. C.O.C.

Inlay Effects on Embossed Fabrics
Joseph Bancroft & Sons Co. *BP* 777,715

Inlay effects of great durability to repeated washings and dry-cleanings are obtained by using as the base of the inlay paste either (*a*) a heat-hardenable alkyd resin and an oil, or (*b*) an oil-modified heat-hardenable alkyd resin, or (*c*)

an oil-modified heat-hardenable alkyd resin and a compatible oil which may be the same or different from that used to modify the resin. C.O.C.

Pleating of Cellulosic Fabrics
P. F. Crosland *BP* 776,195

Fabric impregnated with the precondensate of a resin, dried, pleated with simultaneous or subsequent setting of the resin and then thoroughly washed with mechanical agitation in absence of tension in warp or weft is soft, springy, relaxed and flexible. It has a high degree of resistance to crease and requires much less care before or after being made up into a garment. C.O.C.

Permanent Waving
R. Bessono *BP* 778,729

Addition of not more than 3% of yeast to a cold waving solution speeds up the process and leaves the hair in better condition. C.O.C.

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Transformation of Cellulose at elevated Temperatures. IV—Influence of the Degree of Polymerisation of Cellulose on the Formation of *laevo*-Glucosan
O. P. Golova, A. M. Pakhomov, and I. I. Nikolaeva
Izvestiya Akad. Nauk S.S.S.R. otdel khim. nauk, 519–521 (April 1957)

A change of the cellulose chain length between the limits 150–1000 glucose units, whilst maintaining the physical structure of cellulose, does not affect the yield (59–63%) of *laevo*-glucosan when purified cotton is thermally treated under vacuum. Cellobiose is also investigated. G.J.K.

Sorption and Desorption Kinetics of Water in Regenerated Cellulose
A. C. Newns
Trans. Faraday Soc., **53**, 1150 (Aug. 1957)

Previous studies (*ibid.*, **52**, 1533 (1956)) are extended to the upper limb of the hysteresis loop and within the loop. Kinetics are separated into two stages—a first stage corresponding to diffusion and a second stage interpreted in terms of a slow structural change. The fractional change in concentration of water in the initial stage and the second change rates are very dependent on the initial state of the system. The data may also be explained in terms of changes in polymer structure. W.R.M.

Kinetics of the Formation of Soda Cellulose
A. T. Serkov, E. M. Moguievskii, and A. B. Pakshver
J. Appl. Chem. U.S.S.R., **30**, 309–311 (Feb. 1957)

During the investigation of the kinetics of the interaction of cellulose with aq. NaOH sol. it was shown that the absorption of NaOH by cellulose takes place in two stages. The first stage is completed quickly in 15–60 sec. and results in the take up of 80–90% of total absorbed NaOH by way of convective diffusion, the second slowly, in 60–120 min. by way of molecular diffusion. Therefore the process of combination with NaOH, swelling, evolution of heat and shrinkage of the fibre takes place in two stages. T.Z.W.

Thermal Decomposition of Trimethylcellulose under Vacuum
A. M. Pakhomov, O. P. Golova, and I. I. Nikolaeva
Izvestiya Akad. Nauk S.S.S.R. otdel. khim. nauk, 521–523 (April 1957)

Thermal decomposition of trimethylcellulose under vacuum yields 2:3:6-trimethyl-1:4-anhydro-1:5-glucopyranose; whereas there is no evidence for 2:3:4-trimethyl-1:6-anhydro-1:5-glucopyranose. G.J.K.

Quantity of Carboxyl Groups and its Influence on the Mechanical Properties of Ethylcellulose
O. G. Efremova, I. K. Kos'reva, A. F. Kondrashova, and S. A. Glikman
J. Appl. Chem. U.S.S.R., **30**, 142–148 (Jan. 1957)

The titration of ethylcellulose soln. in acetone with 0·05 N.-NaOH and the reaction with Ba *o*-nitrophenol shows that the ester contains varying No. of carboxyl groups, namely 1 COOH group per 43–111 units of ethylcellulose chain. The acetylation of ethylcellulose brought about by the action of monochloroacetic acid on ethylcellulose soln. in benzene–methyl alcohol in alkali medium maintained by the addition of CH_3COONa, increases the No. of carboxyl groups, causes small decrease in the viscosity and increases the elastic–viscous constants of the gel. The introduction of the small quantities of $Ca(OH)_2$ causes great increase of those constants. Contrary to the influence of the metallic salts of weak acids, chlorides do not exhibit any influence on the elastic-viscous constants of ethylcellulose gel. The addition of metallic hydroxides increases the resistance to tear and decreases the No. of bends at the breaking point of the ethylcellulose film. T.Z.W.

Location and Distribution of Substituents in a Purified Hydroxyethylcellulose
H. H. Brownell and C. B. Purves
Canadian J. Chem., **35**, 677–688 (July 1957)

A hydroxyethylcellulose, freed from uncombined polyethylene glycols by pptn. from aq. soln. with acetone, was completely hydrolysed with 2% hydrochloric acid, and, after de-ionisation, the hydrolysate was resolved by paper chromatography using *n*-butanol saturated with H_2O. The chromatogram gave eight spots corresponding to glucose, 6-, 2- and 3-hydroxyethyl glucose, 2:6-, 3:6- and 2:3-di-(hydroxyethyl)glucose and 2:3:6-tri-(hydroxyethyl)glucose (R_f increasing in this order) as indicated by chromatographic comparison with the synthetic compounds. However, higher homologues, e.g. hydroxyethoxyethylglucoses, could not be resolved. Quantitative determination of the reducing sugars in each spot gave values for the mole fraction of each sugar of—Spot No. 1, 0·4; No. 2, 0·27; No. 3 + 4, 0·12; No. 5 + 6, 0·11; No. 7, 0·06; and No. 8, 0·04. Thus the degree of substitution in the glucose residues is 0·85, giving the average No. of ethylene oxide units per substituent group as 1·6. The mole fractions of sugars indicate that in alkali cellulose the primary hydroxyl group of the anhydroglucose unit reacts fastest and the 3-hydroxyl reacts slowest. A.J.

Radioactive Study of Two-stage Diffusion in the Acetone–Cellulose Acetate System
G. S. Park
Trans. Faraday Soc., **53**, 1149 (Aug. 1957)

Studies of the diffusion of radioactive acetone in acetone–cellulose acetate mixtures suggests that the first stage of the two stage process is a diffusion process in which the driving force for diffusion is given by activities calculated from quasi-equilibrium data. W.R.M.

Acetophthaloyl Ethers of Cellulose
O. M. Klimova and V. A. Bershtein
J. Appl. Chem. U.S.S.R., **29**, 1849–1855 (Dec. 1956)

The action of phthalic anhydride on secondary cellulose in the presence of pyridine results in the formation of mixed aceto-phthaloyl ethers. The amount of phthaloyl groups combined depends upon the conditions of the reaction. When the ratio of the anhydride to the cellulose acetate is 8:1 or more, partial replacement of acetyl groups by phthaloyl takes place. Prolonged heating of the reaction mass causes splitting of the phthaloyl groups. The quantity of acetyl groups does not change. The mixed ethers of cellulose are not stable to prolonged heating at 80–100°C. or above. The mixed ethers are soluble in organic solvents. The films produced from them are transparent and elastic. Presence of a large quantity of free carboxyl groups in the mixed ethers shows the possibility of the formation of three-dimensional derivatives of cellulose. T.Z.W.

PATENTS

Carbon Paper
Gunther Wagner *BP* 779,404

A thin carbon paper with two sides contrasting in colour which remains opaque is achieved by a thermoplastic coating such as polyvinyl acetate on the raw tissue paper intermediate between it and the colour-surrendering layer. An example of the coating is artificial resin (15 parts) dissolved in an organic solvent (25), ground soot (10), the whole being made to 100 parts by addition of spirits. The rear side of the raw tissue is coated with a layer containing pigments and a binding agent, an example in parts by weight being—alcohol soluble synthetic or natural resin (22), red iron oxide (10), red lac dye (15), titanium white (10), methyl alcohol (28), ethylene glycol (15). G.S.B.

Paper composed of Fibres of Polytetrafluoroethylene and other closely related Polymers
DuP *BP* 781,512

An improved acid resistant filter paper manufactured from synthetic resin is obtained from polytetrafluoroethylene and other closely related polymers by extruding

lubricated colloidal particles of these, followed by cutting and shredding operations leading to fibres of improved felting properties. The sheet, which may include inorganic fibres such as asbestos, is subsequently calendered, dried and finally sintered at a temperature of from 350° to 370°C. G.S.B.

Study of Sulphate in Cellulose Nitrate using $^{35}SO_4^{2-}$ as Tracer (VI p. 527)
Effects of Mercerisation on the Lateral Order Distribution of Cellulose (X p. 529)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Keratinisation of Horn

K. M. Rudall

Proc. International Wool Textile Research Conf. Australia, **F**, F 176–F 185, F 222 (1955)

Analysis of the fibrous α-type protein extracted from the inner and the outer mucosum of horn shows an approximate doubling of the sulphur content passing from the inner to the outer layer. There is a further great increase of sulphur passing from the outer mucosum to the keratin layers. Two processes of sulphur accumulation are envisaged: the first by incorporation of more sulphur into protein chains already having the α-keratin structure, and the second by the formation (about the time of keratinisation) of a non-fibrous cementing protein of high sulphur content. The sulphur content of the fibrous protein from the outer mucosum of horn is about the same as that of the high molecular weight fraction obtained from wool which has been dissolved after oxidising the cystine. The sulphur content of the "cutis cornu" is about the same as that of the protein extracted from the inner mucosum of horn. P.G.M.

Finishing Materials for Decorated Leathers

A. Turow

Leather and Shoes, **133**, No. 10, 17 (1957):
J. Amer. Leather Chem. Assocn., **52**, 350 (June 1957)

A discussion of the problems in decorating leather caused by not marking the type of finish used and improper use of finishes. C.J.W.H.

Resin Finishes for Upper Leather

V. Pektor and L. Dvoranek

Kozarstvi, **6**, 87–89 (1956):
J. Amer. Leather Chem. Assocn., **52**, 409 (July 1957)

The elongation at break was measured for 0·1 mm. films of resins, formed by spraying on glass, and the effect of adding other finishing materials was studied. The elongation of a mixture of butyl methacrylate and butyl acrylate (4 : 1) was lowered by adding more than 15% of a casein finish, and with 30% added the film was brittle. Addition of a casein–wax mixture had less effect. The elongation of this resin increased with temperature. The resin is stable to ultraviolet radiation. A pure polyethacrylate film elongated by 1000%, compared to 600% for the butyl acrylate–methacrylate mixture, but the elongation dropped to 448 and 178% respectively when 10 and 20% casein was added. The polyethacrylate elongation was less affected by temperature than that of the butyl polymer. A mixture of polymethacrylate and dibutyl phthalate (9 : 1) showed elongation exceeding 1000%, and elongation was less affected by adding casein or wax–casein than those of the resins previously discussed. In contrast with the previous resins the elongation increased at lower temperatures. Effects of adding white pigments (TiO_2 dispersed with casein) are discussed. Formulas are given for finishing various kinds of leathers. C.J.W.H.

PATENT

Tanning Agents

Boehme Fettchemie *BP* 779,244

The water-soluble products obtained by condensing an organic sulphonamide with an oxo compound, e.g. HCHO, and urea, thiourea, guanidine or a derivative of one of these which contains at least one exchangeable H atom, the molar ratio of the oxo-compound to the sum of the other compounds being $\leq 4:1$, are used as tanning agents. They are applied to the hides and then insolubilised by electrolytes or heat. Their use yields pale or pure white leather of good fullness. C.O.C.

XIII— RUBBER; RESINS; PLASTICS

Formaldehyde Polymer for Industrial Use

G. S. Petrov and V. J. Serenkov

J. Appl. Chem. U.S.S.R., **29**, 1891–1893 (Dec. 1956)

Formaldehyde produced by distillation of the technical formol under 8–12 mm. Hg at 26–32°c. was dissolved in 30% H_2SO_4 soln. in the ratio of 10:6–7. On completion of solution it was allowed to crystallise for 36 hr. Thus a 68% yield of the polymer was obtained, which was filtered off, washed with distilled water, and dried in the air for 24 hr. When the dissolution of formaldehyde was carried out under higher vacuum the yield of the polymer increased to 75%. T.Z.W.

Salt Effects on the Polymerisation of Acrylonitrile in Non-aqueous Solution

C. H. Bamford, A. D. Jenkins, and R. Johnston

Proc. Roy. Soc., **A 241**, 364–375 (20 Aug. 1957)

The polymerisation of acrylonitrile in *NN*-dimethylformamide with added lithium salts is studied. Coefficients for the propagation reaction and transfer reactions to triethylamine and carbon tetrabromide are functions of the concentration and nature of the added salt. Results are interpreted in terms of complex formation between polyacrylonitrile radicals and ions of salt. The termination reaction is not significantly affected by salts. In certain cases, an anionic polymerisation, initiated by salt, is observed. W.R.M.

PATENTS

Rendering Polyethylene Surface strongly adherent to Inks, Lacquers, etc.

Traver Corpn. *BP* 778,803

The surface of the polyethylene, is subject to an electrostatic discharge by placing it together with a glass insulating element between electrodes at different potentials. The discharge is applied to the whole surface via the insulating element with sufficient intensity to render the surface molecules of the polyethylene highly unsaturated. Inks, lacquers, etc. adhere strongly to the treated surface. C.O.C.

Flame-resistant Elastomer Compositions

B. F. Goodrich Co. *BP* 776,807

Incorporation of iodine or an organic material liberating iodine effectively increase the flame resistance of olefinically-unsaturated elastomers. Further increase in flame resistance is given if an inorganic carbonate which liberates CO_2 at 100–500°c. is also present. C.O.C.

Polymerisable Quaternary Ammonium Compounds

Ciba *BP* 777,488

Vinyl ethers containing (*a*) at least one quaternary ammonium group not bound to a hetero-atom through a methylene bridge and (*b*) no other ethylenically unsaturated group but the vinyl ether group, are valuable compounds for making polymers and copolymers suitable for a wide variety of purposes including fibres, textile finishes and lacquers. C.O.C.

Resin Finishes for Upper Leather (XII this page)

XIV— ANALYSIS; TESTING; APPARATUS

Determination of the Strength of Food Dyes

P. Raymond and E. L. K. Dugneaux

Chem. Weekblad, **53**, 134–136 (1957):
Chem. Abs., **51**, 10313 (25 July 1957)

The accepted food dyes in Holland usually contain NaCl or K_2SO_4 and vary from 36·6–94·0% in dye content. Azo, triarylmethane and nitro dyes can be measured by reduction with $TiCl_3$. C.I. Food Red 14 being insoluble in acid media, is determined gravimetrically by precipitation with HCl; for the same reason C.I. Vat Blue 4 is determined by a Kjeldahl N assay. Many commercial food dyes are mixtures. The ratio is found by paper chromatography and the dye content then determined by $TiCl_3$ titration. Presence of C.I. Food Yellow 1 necessitates more exact determination of the ratio in mixtures where it is present as its titre is exceptionally high. C.I. Food Black 1 and C.I. Food Blue 2 have very low titers but are not usually present in such amount as to demand extra care. C.O.C.

Colour Reactions of Vat Dyes, Mainly of Polycondensed Systems and Their Derivatives in Sulphuric Acid. I— Basicity of the Carbonyl Group of Polycondensed Aromatic Amines in Sulphuric Acid
T. Handa and M. Kobayashi
Yôki Gôsei Kagaku Kyokai Shi, **13**, 580–590 (1955)

II— Colour Reactions of Solutions of Condensed Polynuclear Aromatic Hydrocarbons in Sulphuric Acid
T. Handa
Ibid., **14**, 337–343 (1956)

III— Basicities of Condensed Polynuclear Hydrocarbons
Ibid., 550–558:
Chem. Abs., **51**, 8439 (10 June 1957)

I— The colour in sulphuric acid and the basicity of a number of quinone derivatives are: *p*-naphthoquinone, red, −7·5; anthraquinone, yellow, −7·5; naphthacenequinone, red, −8·4; benzonaphthenone, yellow with yellowish green fluorescence, −0·8; benzanthrone, red with reddish orange fluorescence, −3·2; methyleneanthrone, red with reddish orange fluorescence, −3·4; phenanthraquinone, green, −7·1; anthanthrone, dark green, −7·9; 3:10-perylenequinone, red, −5·5; benzoperylenequinone, red with orange fluorescence, −6·0; dianthraquinone, red, −5·0; diphenoquinone, brown, −?; dibenzopyrenequinone, brown, −7·4; anthrone, yellow with slight yellowish fluorescence, −5·5; benzophenone, light yellow, −6·0. Relationship between pH value and condition is discussed.

II— Dibenzopyrene (I), violanthrene (II) and tetracene (III) show specific colour reactions in H_2SO_4. The absorption spectra moved to longer wave lengths. The absorption spectra were measured in various strengths of H_2SO_4. The pK of these compounds −5·0 and −7·4, −5·1 and −6·7, and −6·6 respectively.

III— The following pK values are given: anthracene, −7·8, tetracene −6·6, benzanthracene −7·5, pyrene −8·2, benzopyrene −7·4, dibenzopyrene −5·0 and −7·4, anthanthrene −7·4, perilleno −5·2, benzoperillene −8·3, pyranthrene −7·5, violanthrene A −7·4, violanthrene B −5·1 and −6·8, *meso*naphthodianthrene −6·0, dibenzocoronene −8·7, hexamethylbenzene −5·0. C.O.C.

Quantitative Estimation of Indigoid Dyes on the Fibre
L. M. Golomb
J. Appl. Chem. U.S.S.R., **30**, 329–332 (Feb. 1957)

When a cellulosic textile material coloured with an indigoid or thioindigoid dye is treated, for 30 min. or more, at 20–25°c., with a solution containing 300 ml. of organic solvent, 5 g. NaOH, 10 g. $Na_2S_2O_4$, and made up to 1000 ml. with dist. water, partial or complete stripping of the material takes place. The dye remains in soln. and its concentration can be measured optically. The suitable organic solvents are— ethylene glycol monoethyl ether, triethylene glycol, glycerol, and ethylene glycol. T.Z.W.

Polarographic Analysis of Chromate Pigments
J. Baltes and P. Wiertz
Peintures, Pigments, Vernis, **33**, 222–225 (1957):
Chem. Abs., **51**, 10088 (10 July 1957)

Study of a polarographic method for determining in one operation the main constituents of Pb and Zn chromate pigments. The basic solution, used as a medium, contains equal parts of NH_4Cl, NH_4 citrate and NaOH. A dropping Hg electrode was used together with a "PO_3" polarograph. The detailed procedure is described and the results interpreted. Examples using Pb and Zn chromates are given. Impurities in the pigments can be detected. C.O.C.

X-Ray Determination of Phase Composition of Crystalline Pigments
E. A. Shugan
Khim. prom., 426–428 (1956):
Chem. Abs., **51**, 10088 (10 July 1957)

Work which shows that X-ray testing of TiO_2 pigments for their rutile and anatase content in the factory space dust and in bauxite is effective under industrial conditions. C.O.C.

Powder Reflectometer
H. E. Rose
Paint Technol., **21**, 91 (1957)

An instrument for the rapid determination of the reflectivity characteristics of fine powder. It can also be used to determine the particle size of black powders of particle diameters $< 0{\cdot}5\,\mu$. By calibration against samples of known size it is probable that particle size of coloured powders could also be determined. It is also a convenient means for determination of spectral distribution of light reflected from coloured pigments. It consists of a reflectometer head and a galvanometer unit containing a stabilised power pack for energising the bulb. C.O.C.

Practical Applications of Colorimetry in Industrial Laboratories. I, II
F. Braun
Peintures, Pigments, Vernis, **32**, 750–756, 866–870 (1956)
Chem. Abs., **51**, 10923 (25 July 1957)

Review of methods of colour analysis, photocolorimetric equipment and use of colorimetry in marking and identification of paints. C.O.C.

Application of the Xenon Lamp as a Standard Light Source for Radiation and Colour Measurement
H.-G. Frühling, W. Münch, and M. Richter
Farbe, **5**, 41–68 (Sept. 1956)

A detailed study of the spectral emission of two types of Osram Xenon high-pressure lamps in the visible, infrared, and ultraviolet. The type with small electrode separation shows good constancy and reproducibility. Its advantages as a standard light source for photometry, colorimetry and the evaluation of fluorescent pigments are noted. R.B.B.

Investigation of the Tint of White Pigments using the Concave Cone Multiplier Method
E. A. Becker
Farbe, **5**, 69–73 (Sept. 1956)

The above method is described and some peculiarities considered. R.B.B.

Measurement of Brightening Power of White Pigments (Visual Behaviour)
Farbe, **5**, 78–80 (Sept. 1956)

German standard, based on assessment of brightening power in admixture with a specified blue paste, as compared with that of a lithopone standard mixed with the same blue paste. R.B.B.

Sensitometry of Colour Films
W. Grossmann
Farbe, **5**, 7–22 (Sept. 1956)

Response of the Human Eye to Sudden Changes in Wavelength of Stimulation
W. R. Biersdorf and J. C. Armington
J. Opt. Soc. Amer., **47**, 208–215 (March 1957)

Electroretinograms (ERG) were recorded with a contact electrode on the lens of the human eye and a reference electrode on the forehead. Stimulation changes were studied in which a particular chromatic adaptation stimulus was abruptly replaced by a long duration test stimulus. Adaptation to a particular colour lowered the sensitivity to the same part of the spectrum. Whilst ignorance of the precise origin of the ERG response does not permit definite correlation with receptor activity alone, conclusions may be drawn concerning several independent retinal processes. The present method clearly resolves a spectral process (red process) with a maximum near 620 mμ consistent with the maximum of the cone pigment cyanopsin. Previous experiments with flickering light gave a better resolution than obtained in the present series of the process with a max. between 500 and 550 mμ, a bright light or scotopic red process.

Other processes may contribute to the ERG both in the middle and short wave regions but the sensitivity of the present procedure is insufficient to reveal their maxima. R.B.B.

Spectral Energy Calibration of a Light Flash Source Used in Physiological Experiments
B. Buchmann-Olsen and A. M. Rosenfalck
J. Opt. Soc. Amer., **47**, 30–34 (Jan. 1957)

Test methods and typical performance data are given for the Sylvania glow modulator tube, a flash light source used in colour vision studies. R.B.B.

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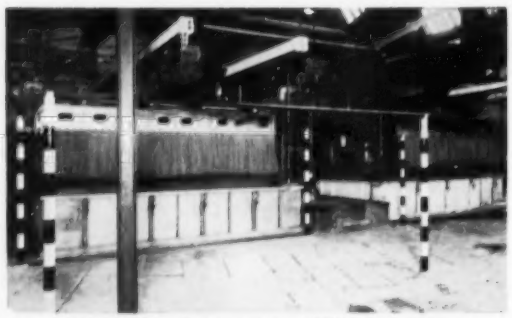
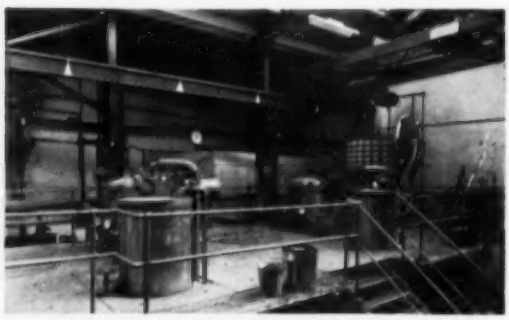


Carpet Yarn Dyeing unit—4/5000 lb. capacity



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FORTHCOMING MEETINGS OF THE SOCIETY—*continued from page viii*

Friday, 7th February 1958

LONDON SECTION. *Spun-dyed Fibres, their Properties and Uses.* C. C. Wilcock, Esq., A.R.T.C.S., F.T.I., F.S.D.C. (Courtaulds Ltd.). Royal Society, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 11th February 1958

BRADFORD JUNIOR BRANCH. *The Role of Optical Whitening Agents.* C. Fearnley, Esq., B.Sc., Ph.D. (Geigy Co. Ltd.). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

NORTHERN IRELAND SECTION. *A New Approach to Pigment Dyeing.* T. Weber, Esq. (Ciba Limited). Further details later.

Thursday, 13th February 1958

MANCHESTER JUNIOR BRANCH. *The Scientific Background to Mangling.* E. Moss, Esq. Room C9, Manchester College of Technology, **Manchester.** 4.30 p.m.

MIDLANDS SECTION. *A New Approach to the Pigment Dyeing of Piece Goods.* T. Weber, Esq. (Ciba Ltd, Basle). Gas Board Theatre, **Nottingham.** 7 p.m.

WEST RIDING SECTION. *Investigations on the Dyeing Process of Polyester Fibres with Disperse Dyes.* Dr. Glenz (Bayer Co., Leverkusen). Metropole Hotel, King Street, **Leeds.** 7.30 p.m.

Tuesday, 18th February 1958

HUDDERSFIELD SECTION. *The Continuous Dyeing of Wool.* D. R. Lemin, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *A New Approach to Pigment Dyeing of Piece Goods.* Lecturer to be announced later. St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Thursday, 20th February 1958

BRADFORD JUNIOR BRANCH. Annual Dance. Fountains Hall, **Bradford.**

Friday, 21st February 1958

MANCHESTER SECTION. *The Application of Acrylonitrile in the Textile Industry.* J. H. MacGregor, Esq., Ph.D., F.R.I.C. (Courtaulds Ltd., Textile Research Laboratory, Bocking). The Textile Institute, 10 Blackfriars Street, **Manchester 3.** 7 p.m.

Thursday, 27th February 1958

WEST RIDING SECTION. J. B. Speakman. Esq., D.Sc., F.R.I.C., F.T.I. Details later.

Tuesday, 4th March 1958

LEEDS JUNIOR BRANCH. *Optical Bleaching Agents.* D. A. W. Adams, Esq., Ph.D. Department of Colour Chemistry and Dyeing, The University, **Leeds 2.** 3.15 p.m.

Friday, 7th March 1958

BRADFORD JUNIOR BRANCH. *The Dyeing of Cellulosic Fibres with Alcian X Dyestuffs.* J. T. Turner, Esq. (I.C.I. Ltd.). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

LONDON SECTION. *Recent Developments in the Dyeing of Man-made Fibres.* Dr. R. Wittwer (Ciba Ltd.). Royal Society, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 11th March 1958

HUDDERSFIELD SECTION. *Recent Developments in the Dyeing of Man-made Fibres.* Lecturer to be announced later. Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

NORTHERN IRELAND SECTION. *Some Observations in the Uses of Synthetic Resin Products and Chemical Reactants to Cellulosic Materials.* F. Sloan, Esq., M.Sc. (Kirkpatrick Bros. Ltd.). Further details later.

Thursday, 13th March 1958

MANCHESTER JUNIOR BRANCH. *Terylene.* J. R. Whinfield, Esq. Room C9, Manchester College of Technology, **Manchester.** 4.30 p.m.

WEST RIDING SECTION. Discussion, *Fluorescent Brightening Agents.*

Panel
- A Member of the British Cotton Industries Research Association.
- J. S. Ingham, Esq. (Marks & Spencer Ltd.).
- Dr. Fearnley (Geigy Co. Ltd., Manchester).
- J. Rayment, Esq. (G. & W. N. Hicking).

Victoria Hotel, **Bradford.** 7.30 p.m.

Tuesday, 18th March 1958

SCOTTISH SECTION. *Easy-care Finishes on Fabrics Containing Courpleta, with Special Reference to Pleating, Embossing and Setting.* A. S. Cluley, Esq., F.T.I. and S. N. Bradshaw, Esq. (Courtaulds Ltd., Coventry). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Wednesday, 19th March 1958

MIDLANDS SECTION. *Optical Brightening Agents.* D. A. W. Adams, Esq., B.Sc., Ph.D. (Joint meeting with The British Association of Chemists.) Midland Hotel, **Derby.** 7 p.m.

Friday, 21st March 1958

MANCHESTER SECTION. One-day Symposium. *New Information on Finishing Processes.* Manchester College of Science and Technology, **Manchester.**

MIDLANDS SECTION. Section Annual Dinner. George Hotel, **Nottingham.**

Tuesday, 25th March 1958

HUDDERSFIELD SECTION. Annual General Meeting.

Thursday, 27th March 1958

BRADFORD JUNIOR BRANCH. *Continuous Dyeing of Wool.* D. R. Lemin, Esq., B.Sc. (I.C.I. Ltd.). Bradford Institute of Technology, **Bradford.** 7.15 p.m.

WEST RIDING SECTION. Annual General Meeting. Victoria Hotel, **Bradford.** 7.30 p.m.

Saturday, 29th March 1958

BRADFORD JUNIOR BRANCH. Annual General Meeting. Bradford Institute of Technology, **Bradford.** 10.15 a.m.

Thursday, 3rd April 1958

MIDLANDS SECTION. *Recent Trends in Dyeing for the Carpet and Hosiery Trades.* W. Beal, Esq., B.Sc. (Geigy Co. Ltd.). Messrs. Carpet Trades Ltd. Canteen, Mill Street, **Kidderminster.** 7.30 p.m.
(Joint with the Textile Institute, Kidderminster Section).

Wednesday, 16th April 1958

MIDLANDS SECTION. *Basic Principles of Dyeing with Disperse Dyes.* D. Finlayson, Esq., M.C., M.A., D.Sc. and H. C. Olpin, Esq., M.Sc., F.R.I.C., F.S.D.C. King's Head Hotel, **Loughborough.** 7 p.m. (Preceded at 6.30 p.m. by the Annual General Meeting of the Section.)

Friday, 18th April 1958

LONDON SECTION. *Colour Fastness Requirements of Luton Textiles.* I. Glasman, Esq., A.T.I. (Marks & Spencer Ltd.). George Hotel, **Luton.** 7 p.m.

MANCHESTER SECTION. Annual General Meeting. Details to be announced later.

Friday, 2nd May 1958

LONDON SECTION. Annual General Meeting and Dinner. Aldwych Brasserie, Aldwych, **London, W.C.2.** 6 p.m. for 6.30 p.m. (Mr. C. O. Clark will speak on the standards required for the A.S.D.C. examination.)

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the twelve labours

Minos, King of Crete, an Island south of Greece, had once promised to sacrifice a huge bull to Neptune, the God of the Sea. Because of its great size and beauty, however, Minos had kept it for himself. The bull went mad and began to destroy the crops of the island.

Hercules, with his customary resolution and dependability, completed his seventh labour by capturing the raging beast alive and bringing it to Mycenae. Unfortunately, King Eurystheus foolishly let it loose and it crossed the Isthmus of Corinth and ravaged the valley of Marathon, in Attica.

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All inquiries relating to Advertisements should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

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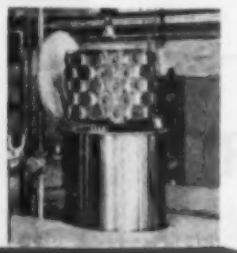

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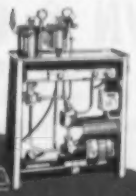

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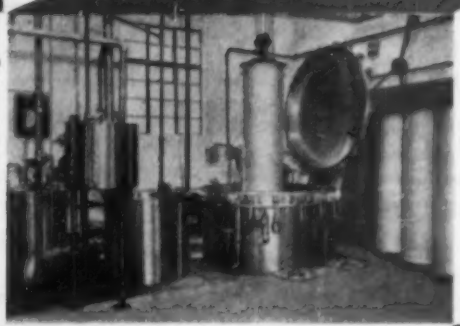

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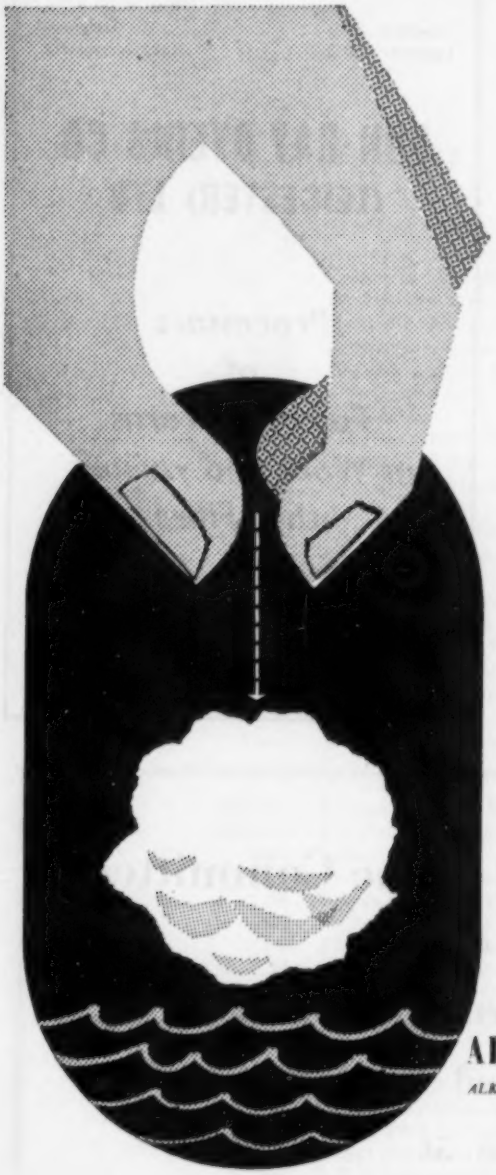

Polyphosphates in kier boiling

At a bleachworks producing cotton wool, the finished material was sometimes unsatisfactory when tested for absorbency. Polygon (sodium tripolyphosphate) added to the kier liquor solved this problem. The sequestering and dispersing properties of the polyphosphate enabled a cotton wool to be produced with a minimum of impurities.

This is only one example of the value of using a polyphosphate in the kier. Another is in kier-boiling cotton cloth where polyphosphates will reduce kier stains, sequester the metallic ions, which can cause degradation of the cotton fibre, and dissolve insoluble metallic soaps. The introduction of polyphosphate ensures a cleaner cloth and reduces re-processing.

For further information about Albright & Wilson's polyphosphates–Calgon (glassy sodium metaphosphate), Polygon* (sodium tripolyphosphate) and Tetron* (tetrasodium pyrophosphate), write to:*

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